NBS MONOGRAPH 110

Infrared Spectroscopy Of Carbohydrates

A Review of the Literature

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards[1] provides measurement and technical information services essential to the efficiency and effectiveness of the work of the Nation's scientists and engineers. The Bureau serves also as a focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To accomplish this mission, the Bureau is organized into three institutes covering broad program areas of research and services:

THE INSTITUTE FOR BASIC STANDARDS . . . provides the central basis within the United States for a complete and consistent system of physical measurements, coordinates that system with the measurement systems of other nations, and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. This Institute comprises a series of divisions, each serving a classical subject matter area:

—Applied Mathematics—Electricity—Metrology—Mechanics—Heat—Atomic Physics—Physical Chemistry—Radiation Physics—Laboratory Astrophysics[2]—Radio Standards Laboratory,[2] which includes Radio Standards Physics and Radio Standards Engineering—Office of Standard Reference Data.

THE INSTITUTE FOR MATERIALS RESEARCH . . . conducts materials research and provides associated materials services including mainly reference materials and data on the properties of materials. Beyond its direct interest to the Nation's scientists and engineers, this Institute yields services which are essential to the advancement of technology in industry and commerce. This Institute is organized primarily by technical fields:

—Analytical Chemistry—Metallurgy—Reactor Radiations—Polymers—Inorganic Materials—Cryogenics[2]—Office of Standard Reference Materials.

THE INSTITUTE FOR APPLIED TECHNOLOGY . . . provides technical services to promote the use of available technology and to facilitate technological innovation in industry and government. The principal elements of this Institute are:

—Building Research—Electronic Instrumentation—Technical Analysis—Center for Computer Sciences and Technology—Textile and Apparel Technology Center—Office of Weights and Measures —Office of Engineering Standards Services—Office of Invention and Innovation—Office of Vehicle Systems Research—Clearinghouse for Federal Scientific and Technical Information[3]—Materials Evaluation Laboratory—NBS/GSA Testing Laboratory.

---

[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D. C. 20234.

[2] Located at Boulder, Colorado 80302.

[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

UNITED STATES DEPARTMENT OF COMMERCE
C. R. Smith, *Secretary*
NATIONAL BUREAU OF STANDARDS • A. V. Astin, *Director*

Infrared Spectroscopy of Carbohydrates

A Review of the Literature

R. Stuart Tipson

Institute for Materials Research
National Bureau of Standards
Washington, D.C. 20234

National Bureau of Standards Monograph 110

Issued June 1968

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 - Price 30 cents

Library of Congress Catalog Card Number: 68-60029

Contents

Infrared Spectroscopy of Carbohydrates

A Review of the Literature

R. Stuart Tipson [1]

A survey has been made of the literature on the infrared spectroscopy of carbohydrates, in order to assemble and systematize information in this field. The Monograph discusses principles and instrumentation, sampling techniques, comparison of samples, and the interpretation of the spectra, particularly as regards functional groups of carbohydrates and their derivatives, correlations for the fingerprint region and beyond, and conformational studies. In addition, examples are discussed of the use of infrared spectra for qualitative and quantitative purposes and in the determination of structure. Special techniques are briefly described, including use of plane-polarized radiation, the technique of attenuated total reflection, and Raman spectra.

Key Words: Analysis, carbohydrates, conformations, infrared spectra, spectrometry, structure.

1. Introduction

Although a large number of books on the infrared spectroscopy of organic compounds have been written [1],[2] detailed attention has not been accorded in them to carbohydrates and their derivatives. Several books contain chapters on the subject, but these chapters are no longer up to date, and contain certain statements that are open to misinterpretation. Consequently, it was decided that a detailed survey should be made of the literature on the infrared spectroscopy of the carbohydrates and their derivatives, and that the information should be assembled in a readily available form.

2. Principles and Instrumentation

A molecule can exist in a number of energy levels, and a change from one level to another can result from absorption, or in emission, of energy, if selection rules permit this. Of the three kinds of molecular spectra, namely, electronic, rotational, and vibrational, the last kind are obtained when absorption of radiant energy causes changes in the energy of molecular vibration. Most of the vibrational absorption bands [1] are found in the range [3] from 2 to 100 μm (5000 to 100 cm^{-1}); but, as the spectrometers usually available to the organic chemist cover the range of 2 to 40 μm (5000 to 250 cm^{-1}), discussion of infrared spectra will be confined to this range The range of most interest to the carbohydrate chemist is 2 to 15 μm (5000 to 667 cm^{-1}).

Accurate recordings of spectra may be obtained with a recording, double-beam, infrared spectrophotometer equipped with a prism [*e.g.*, of sodium chloride for the range of 2 to 15 μm (5000 to 667 cm^{-1})] or a grating. In such instruments, the sample is exposed to infrared radiation, and that radiation passing through the sample is resolved with the prism or grating; the spectrum is then scanned, and the values (bands) at which radiation is absorbed are recorded, providing an infrared absorption spectrogram. For measurement of bands in the region of 2.7 to 3.6 μm (3700 to 2780 cm^{-1}), the higher dispersion given by a lithium fluoride prism or a comparable grating is an asset. Instead of a suitable grating, a prism of potassium bromide may be used for the range of 2 to 25 μm (5000 to 400 cm^{-1}), and a prism of cesium bromide for 15 to 40 μm (667 to 250 cm^{-1}).

For rapid, routine recording of useful but less accurate spectra, smaller (and cheaper) prism instruments are available as an analytical tool. In the range of 10 to 15 μm (1000 to 667 cm^{-1}),

[1] The author thanks Frank S. Parker, of the Department of Biochemistry, New York Medical College, New York, and James E. Stewart, of Beckman Instruments, Inc., Fullerton, California, for a number of helpful suggestions. This Monograph is, in part, an outgrowth of a comprehensive investigation of the infrared absorption spectra of sugars and sugar derivatives begun at the National Bureau of Standards in 1949. The early work, sponsored by the Office of Naval Research, was conducted by E. C. Creitz, H. L. Frush, H. S. Isbell, J. D. Moyer, F. A. Smith, J. E. Stewart, and R. S. Tipson.

[2] Figures in brackets indicate the literature references at the end of this Monograph.

[3] The position of a band in this region of the spectrum is expressed in two ways: (a) as the wavelength (λ) in μm [micrometers; 1 $\mu m = 10^{-6} m$, commonly called microns (μ)], or (b) as the wavenumber (ν) in reciprocal centimeters (kaysers). The velocity of light (c, in cms^{-1}) is equal to the wavelength of one vibration times the number of vibrations per second; that is, $c = \lambda\nu$. The wavenumber is the reciprocal of the wavelength; thus, ν (in cm^{-1}) $= 1/\lambda$ (in cm), or ν (in cm^{-1}) $= 10^4/\lambda$ (λ in μm). Wavenumbers have the advantage of being directly proportional to energy. As instruments are now available that record linearly either in wavelength or wavenumber, bands will be expressed in both ways in this Monograph.

such an instrument can routinely give wavenumbers accurate to ± 2 cm^{-1}. In the range of 2.5 to 10 μm (4000 to 1000 cm^{-1}), the inaccuracy is increasingly greater with increasing wavenumber; nevertheless, the reproducibility is satisfactory.

3. Sampling Techniques

3.1. Phase

For recording the infrared spectrum, a carbohydrate or derivative may be prepared as (a) a thin layer of an anhydrous syrup mounted between windows that are transparent to the infrared radiation; (b) a mull with a hydrocarbon oil (Nujol [4]) or an appropriate perhalogenated hydrocarbon, mounted in the same way; (c) a pellet made with an alkali-metal halide; or (d) a solution in an organic solvent or water (in a suitable, water-insoluble cell). Recording is usually done with the sample at room temperature, but bands may be sharper at lower temperatures.

The spectrum of a compound may be different for different physical states. For example, in the solid state, polymorphs of a compound, examined in the same way, may show differences in a few features of their spectra. An example is *N*-benzoyl-2,3,4,6-tetra-*O*-benzoyl-β-D-glucosylamine; this exists in a form of mp 113–115 °C which, when heated to 117–120 °C and allowed to crystallize from the melt, gives a form of mp 184 °C having a somewhat different spectrum (Nujol mull). Also, different crystal habits (same mp) of a compound (resulting, for example, from crystallization of samples from different solvents) may give somewhat different spectra, particularly if examined as mulls (where but little pressure is applied). Shifts of up to 20 cm^{-1} for certain bands have been noted [3] for crystalline and amorphous forms of some carbohydrates. However, in all such instances, samples of each of the forms, measured after dissolution in the same solvent, or as molten material, give identical spectra. The spectra of crystalline materials often show more bands than the same compounds in solution [4].

Band positions may be shifted, or band intensities altered, if the compound forms hydrogen bonds with the solvent. In solution, molecules of a compound may associate through formation of intermolecular hydrogen bonds. If the concentration is below 0.005 *M*, intermolecular hydrogen-bonding is negligible for solutions in carbon tetrachloride and similar solvents [5, 6]; this effect has been used in studying intramolecular hydrogen-bonding in model compounds related to sugars [7].

Pelleting of certain free sugars with an alkali halide changes a crystalline sample to an amorphous form [8, 9]. Moreover, some sugars (for example, α-D-glucose) may form a complex with traces of sodium bromide or sodium iodide present in pellets of the corresponding potassiuun halide [9]. If the pelleting halide is not dry [10], or acquires moisture, the sugar may mutarotate or form a hydrate should the pellet be stored [11]. Consequently, such spectra should always be compared with those obtained for a Nujol mull of the compound, or the pellets should not be stored. However, even though examined immediately after preparation of the pellets, eight of 24 aldopyranosides [12] showed interaction with the pelleting halide, and six of 27 free sugars [13] gave spectrograms that were different in Nujol and in potassium iodide.

3.2. Comparison of Samples

As a result of recording and comparing the infrared spectra of a large number of organic compounds, it has been found that every compound having a unique structure gives a unique spectrum. Consequently, for an enantiomorphic pair, every detail of whose structure is identical (but in mirror image), the spectra of the solids, in the same polymorphic modification, are identical [3]. The spectra may differ slightly because of polymorphism, but, for the gaseous or liquid (melt, or solution) phases, the spectra are identical.

Also, for a large molecule, a slight change in structure may change the spectrum only slightly. Thus, proceeding up a series of oligosaccharides containing the same anomeric form of the same monosaccharide residue only, the spectra for the tetraose, pentaose, hexaose, etc., become more and more alike [14].

Consequently, with these exceptions, pure compounds can be identified unequivocally by their infrared spectra. For a carbohydrate, the infrared spectrum is usually a much more specific and characteristic property than the ultraviolet spectrum, melting point, boiling point, density, or refractive index. Thus, although the anomers of a sugar or glycoside differ only in the orientation at one carbon atom, their spectra are quite different [14]. Also, the spectrum of the furanoid form of a sugar derivative differs from that of the pyranoid form in the same anomeric modification, as with methyl β-D-ribofuranoside and β-D-ribopyranoside [15].

Hence, the simplest use of infrared spectra is for the identification of a compound. The spectrum of a sample to be identified is compared with the spectra of pure compounds of known structure, measured with the same sampling technique. In this use, it is not necessary that the spectra be analyzed for characteristic absorption bands. However, availability of reference spectra [16–20] of related, pure compounds is essential.

Another use is the precise identification of spectra already in the literature, where the compound studied had been inadequately described. For example, in 1950, Kuhn [14] recorded the spectra of 10 of the crystalline sugars, each in a

[4] Mention of a commercial product in this article does not constitute endorsement by the National Bureau of Standards.

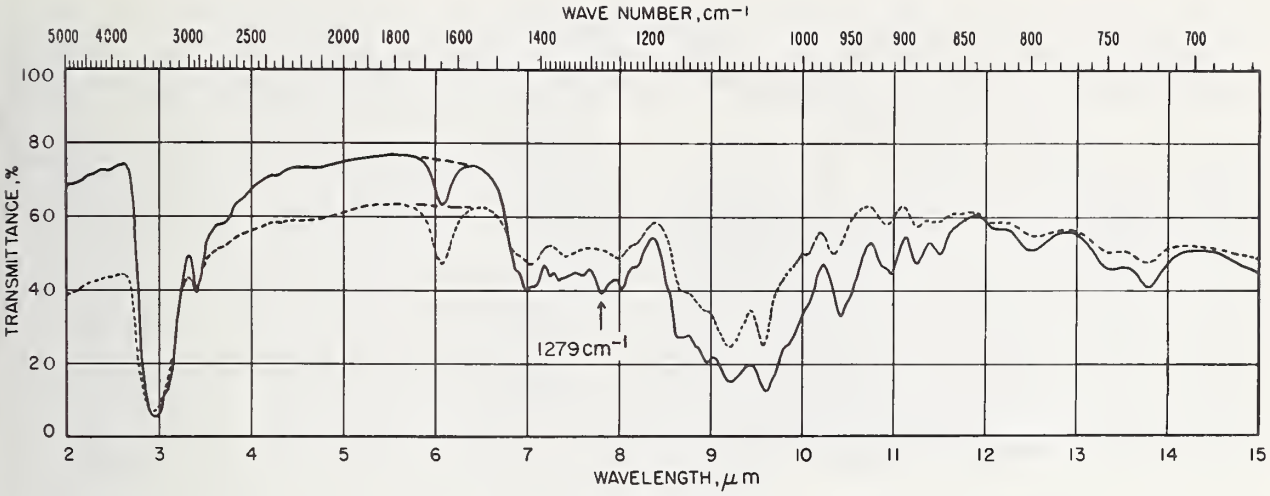


FIGURE 1. *Infrared spectra of commercial* (– – –) *and purified* (——) *β-D-ribose* [13] *in potassium chloride pellets.*

[The band at 6.18 μm (1618 cm⁻¹) is caused by moisture in the compound, the alkali halide, or both.]

Nujol mull; but, except for one (α-D-glucose), he did not mention which anomer had been employed. Similarly, Urbański et al. [21] recorded the spectra of six sugars, without specifying the anomeric form. These have since been identified [13] by comparison with the spectra of authentic anomeric forms of those sugars.

In another application, infrared spectra can be used for checking the purity of a sample. Commonly, a crude material may show a band that is not present in the spectrum of the pure compound; thus, commercial D-mannitol showed a band at 12.80 μm (781 cm^{-1}), due to D-glucitol, removable by recrystallization from aqueous ethanol [22]. In contrast, figure 1 shows the spectrum of pure crystalline β-D-ribose [13] and that of a commercial specimen. The spectrum of the commercial material does not display a band at 7.82 μm (1279 cm^{-1}) that is present in the spectrum of the pure sugar, presumably because presence of impurity causes poor growth of the crystals, resulting in scattering.

The same figure also serves to illustrate that the spectra may be used in following the isolation or purification of a desired product obtained, for example, by distillation or chromatography. It is not necessary to know what the compound is (nor, initially, to have an infrared spectrum of the pure compound); the concentration or purification procedure can be followed by observing some characteristic infrared band. For example, by recrystallizing β-D-ribose until the band at 7.82 μm (1279 cm^{-1}) appears and remains of constant intensity, a sample that is "pure" (by infrared spectroscopy) is obtained, without any knowledge of the actual significance of this band. However, the minimum detectable amount of impurity (which may, of course, contribute bands absent from the spectrum of the pure material) varies enormously from one compound to another.

4. Interpretation of Spectra

4.1. General

A more sophisticated use of infrared spectra permits qualitative analysis for groups of atoms. The motions constantly undergone by the atoms and bonds of a molecule may be examined with a model consisting of springs and balls. A diatomic molecule A—B may be represented by two balls, each of a mass proportional to those of atoms A and B, respectively, connected by a spring of strength proportional to the force binding atoms A and B. Molecule A—B can undergo a stretching vibration only along the bond between atoms A and B; this vibration occurs in the model if the spring is compressed and then the assemblage is permitted to relax on its own. If the resulting, periodic oscillation is moderate, the system follows Hooke's law approximately, and the frequency (ν) of the stretching vibration is given by the equation for simple harmonic vibrations namely $\nu=(f/\mu)^{1/2}/2\pi c$, where f is the force constant of the bond, c is the velocity of light, and μ is the reduced mass, defined as $\mu=m_A m_B/(m_A+m_B)$, where m_A and m_B are the masses of atoms A and B, respectively. (The equation for ν applies only to the example considered.)

For a polyatomic molecule, there are many ways in which pairs of atoms may bend, rock, twist, or vibrate, relative to each other and to other pairs, or larger groups, of atoms. Although a mathematical treatment of the infrared spectrum of any pure compound could provide information on the structure through checking of consistency with possible models, the degree of difficulty of such a calculation is a function of the number of atoms and of the symmetry of their geometrical arrangement. Thus, for most sugars, such a treatment would be very difficult, particularly in

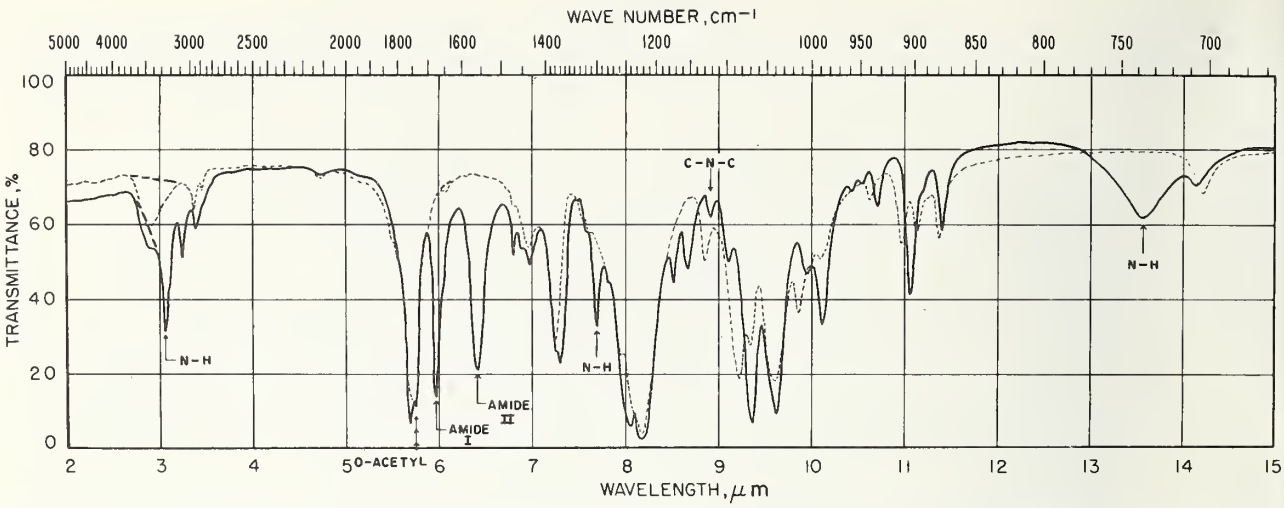


FIGURE 2. *Infrared spectra of 1,2,3,4-tetra-*O*-acetyl-β-*D*-xylopyranose* (– – –) *and of* N*-acetyl-2,3,4-tri-*O*-acetyl-β-*D*-xylopyranosylamine* (——) *in potassium chloride pellets.*

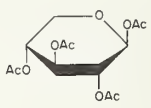
(From Refs. [19] and [20].)

view of additional complications introduced by study of condensed phases.

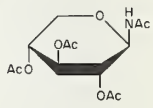
Consequently, in attempting to correlate the structure of the molecule with the frequencies observed in its infrared spectrum, use has been made of the empirical approach. The method is based on the assumption (not necessarily justified) that the vibrations of a certain group are fairly independent of the rest of the molecule. Then, the spectra (recorded under like conditions) of a large number of compounds having this group are examined, to find out which bands the spectra have in common. For example, the spectra of 24 acetylated glycosides were studied [18], together with those for 21 nonacetylated glycosides [12]. It was then obvious that (1) all of the acetates showed a band at 5.64 to 5.76 μm (1773 to 1736 cm^{-1}; C=O stretching frequency) not shown by any of the nonacetylated compounds; and (2) all of the nonacetylated glycosides, but not the acetates, showed a band at 2.93 to 3.05 μm (3413 to 3279 cm^{-1}; —O—H stretching). Furthermore, all of the hydrates (but no anhydrous compounds) showed a band at 6.01 to 6.12 μm (1664 to 1634 cm^{-1}). Here, attention was paid only to the positions of absorption bands, regardless of their relative intensities.

In figure 2 are shown the spectra of 1,2,3,4-tetra-*O*-acetyl-β-D-xylopyranose (**1**) [20] and of *N*-acetyl-2,3,4-tri-*O*-acetyl-β-D-xylopyranosylamine (**2**) [19], compounds that differ by only one connecting atom. In compound **1**, C-1 bears an oxygen atom to which is attached an acetyl group, whereas C-1 of compound **2** bears a nitrogen atom to which is attached a hydrogen atom and an acetyl group. Some differences in the spectra are indicated in figure 2, and are discussed in section 4.

It has been found that, in the absence of disturbing effects, all compounds containing the



1



2

same group will absorb infrared radiation at almost the same wavelength. Thus, bands that occur in the region from 2.0 to *ca.* 7 μm (5000 to *ca.* 1430 cm^{-1}) are usually characteristic group-frequencies; for these, the associated vibration is well localized, as in C=O and X—H stretching vibrations. The precise positions of such bands are more reliable for determining the presence of groups than are bands in the region of 7 to 15 μm (1430 to 667 cm^{-1}). The latter interval, or the interval from 7 to 11 μm (1430 to 910 cm^{-1}), is commonly referred to as the "fingerprint region," because it is usually rich in bands that collectively provide a pattern of bands characteristic of the compound; however, the origin of the bands in the fingerprint region is often not readily determined, and so a detailed study of this part of the spectrum is generally deferred until the rest of the spectrum has been examined. Bands in the region of 7 to 15 μm (1430 to 667 cm^{-1}) may arise from single-bond, skeletal stretching-vibrations (between atoms of similar, or the same, mass) or from bending vibrations. The latter occur in this region because less energy is required to produce them; certain of these bands have diagnostic value for groups, but most of them are greatly influenced by structural changes in the molecule. For carbohydrates and their derivatives, the region of 8 to 10 μm (1250 to 1000 cm^{-1}) contains bands for —C—O— of esters, ethers, and hydroxyl groups, and may not show highly individual bands for such structures.

Some group absorptions may be quite different in intensity from one compound to another, even though the wavelength of the absorption is about the same. However, for small molecules, the bands for carbonyl groups are nearly always very strong. If a spectrum has only a weak band in the region of 5.88 μm (1700 cm^{-1}), (a) this band is probably not due to carbonyl, (b) the molecule is probably very large and has, perhaps, only one carbonyl group, or (c) a carbonyl compound is possibly present as an impurity. Because of the possibility of interference by other absorptions, the presence of a band at a position expected for a certain group is not conclusive evidence that that group is present *in the compound*. However, provided that effects (such as hydrogen bonding) that could shift or even remove the band are not operative, the absence of a group absorption usually indicates absence of that group from the sample.

4.2. Functional Groups in Carbohydrates and Their Derivatives

Except when electrical (hydrogen bonding, ionization, etc.) or steric effects are operative, every organic compound that possesses a particular group will show the corresponding, characteristic group-frequency in its spectrum, and many compilations of such group-frequencies are available [1]. Table 1 lists the group frequencies in which the sugar chemist is likely to be interested, and provides an estimate of their relative intensities; about half of the characteristic group-frequencies lie in the range of 2 to 7 μm (5000 to 1430 cm^{-1}) and the rest above 7 μm (below 1430 cm^{-1}).

TABLE 1. *Characteristic infrared bands shown by various groups*

Range		Intensity [a]	Group	Type of vibration [b]	Remarks
μm	cm^{-1}				
2.22–2.38	4505–4200	w	C—H	str.	aliphatic (combination)
2.35–2.50	4255–4000	w	C—H	str.	aromatic (combination)
2.74–2.86	3650–3500	var	O—H	str.	free OH, oxime
2.75–2.76	3640–3623	m(sharp)	O—H	str.	free OH, alcohols
2.78–3.23	3600–3100	m	O—H	str.	water of crystallization
2.79–2.92	3590–3425	var(sharp)	O—H	str.	intramolec. bonded OH
2.82–2.86	3550–3500	m	O—H	str.	free OH, carboxylic acid (v. dil. soln.)
2.82–2.90	3550–3450	var(sharp)	O—H	str.	intermolec. bonded OH (dimeric)
2.82–3.13	3550–3195	w	C=O	str.	carbonyl (first overtone)
~2.84	~3520	s	N—H	str.	primary amide (free)
~2.86	~3500	m	N—H	str. (asym.)	primary amine, free NH (dil. soln.)
2.86–3.03	3500–3300	m	N—H	str.	secondary amine, free NH
2.86–3.27	3500–3060	m	N—H	str.	associated NH, amine or amide
~2.94	~3400	s	N—H	str.	primary amide (free)
~2.94	~3400	m	N—H	str. (sym.)	primary amine, free NH (dil. soln.)
2.94–3.10	3400–3225	s(broad)	O—H	str.	intermolec. bonded OH (polymeric)
~2.96	~3380	m	NH_3^+	str.	amine salt (soln.)
2.98–3.18	3355–3145	m	NH_3^+	str.	amine salt (solid); several bands
~2.99	~3350	m	N—H	str.	primary amide (bonded)
~3.03	~3300	s	C—H	str.	≡C—H, acetylenes
3.03–4.00	3300–2500	w(v broad)	O—H	str.	H-bonded carboxylic acid dimers
~3.05	~3280	m	NH_3^+	str.	amine salt (soln.)
~3.15	~3175	m	N—H	str.	primary amide (bonded)
3.17–3.28	3155–3050	w	C—H	str.	—CH=C—O— and —C=CH—O—
3.23–3.25	3095–3075	m	C—H	str.	$RCH=CH_2$, olefin
3.25–3.30	3075–3030	w–m	C—H	str.	C—H of aromatic ring
3.28–3.34	3050–2995	w	C—H	str.	of epoxide (shifts to 3040–3030 if ring strain increases)
3.29–3.32	3040–3010	s;m	C—H	str.	≥C—H; $RCH=CH_2$, RCH=CHR′ (*cis* or *trans*), RCR′=CHR″, olefin
~3.38	~2960	s	C—H	str. (asym.)	*C*-methyl
~3.42	~2925	s	C—H	str. (asym.)	$>CH_2$, methylene, Ar—CH_3
3.45–3.47	2900–2880	w	C—H	str.	C—H, methine
3.45–3.70	2900–2705 (two)	w	C—H	str.	—C(=O)H, aldehyde
3.45–4.35	2900–2300 (several)	w	N—H	str.	quarternary amine salt, bonded
~3.48	~2875	s	C—H	str. (sym.)	*C*-methyl
~3.51	~2850	s	C—H	str. (sym.)	$>CH_2$, methylene
3.53–3.55	2835–2815		C—H	str.	*O*-methyl

See footnotes at end of table.

TABLE 1. *Characteristic infrared bands shown by various groups*—Continued

Range		Intensity [a]	Group	Type of vibration [b]	Remarks
μm	cm^{-1}				
~3.54	~2825	m	C—H	str.	$-CH(OCH_2-)_2$, alkyl acetal
~3.60	~2780		C—H	str.	$-O-CH_2-O-$
3.70–3.91	2705–2560	w(broad)	P—OH	str.	phosphoric ester, H-bonded
3.70–4.35	2705–2300	s	NH_2^+, NH^+	str.	(may be several bands)
~3.88	~2580	w	S—H	str.	thiol, free
~4.17	~2400	w	S—H	str.	thiol, H-bonded
~4.41	~2270	vs	N=C=O	asym. str.	isocyanate
4.42–4.46	2260–2240	w	—C≡N	str.	satd. nitrile
4.42–4.57	2260–2190	var	C≡C		RC≡CR′; acetylenes
4.48–4.51	2230–2215	s	—C≡N	str.	unsatd. conj. nitrile
4.55–4.88	2200–2050	vs	C=S	asym. str.	—N—C=S, isothiocyanate (2 or more bands)
4.55–5.00	2200–2000	s			cyanide, thiocyanate, cyanate
4.59–4.72	2180–2120		C≡N	str.	$R-\overset{+}{N}\equiv\overset{-}{C}$
4.63–4.72	2160–2120	s	N≡N	str.	azide
4.67–4.76	2140–2100	w	C≡C		RC≡C–H; acetylenes
~5.53	~1810	s	C=O	str.	—COCl, aliphatic acid chloride
5.62–5.75	1780–1740	s	C=O	str.	—O—(C=O)—O—, carbonate
~5.65	~1770	s	C=O	str.	γ-lactone
5.73–5.76	1745–1735	s	C=O	str.	satd. esters
~5.75	~1740	s	C=O	str.	δ-lactone
5.75–5.81	1740–1720	s	C=O	str.	—C(=O)H, aldehyde
~5.80	~1725	s	C=O	str.	formic ester
5.80–5.87	1725–1705	s	C=O	str.	ketone
~5.81	~1720	s	C=O	str.	benzoic ester
5.81–5.88	1720–1700	s	C=O	str.	—COOH; aliphatic carboxylic acid (dimer)
5.88–5.99	1700–1670	s	C=O	str.	—CONHR, secondary amide, free (dil. soln.): Amide I
5.92–5.99	1690–1670	s	C=O	str.	$-CONH_2$, primary amide, free (dil. soln.): Amide I
5.95–6.14	1680–1630	s	C=O	str.	secondary amide (solid)
5.95–6.17	1680–1620	var	C=C	str.	nonconjugated C=C
5.96–5.99	1678–1668		C=C		*trans* olefin; RHC=CHR′
~5.97	~1675	s	C=S	str.	thioester
~5.97	~1675	s	C=O	str.	thioester
~5.99	~1670	w	C=N	str.	aliphatic oxime
5.99–6.17	1670–1620	s	C=O	str.	primary amide (solid), H-bonded, 2 bands: Amide I
6.02–6.05	1662–1652		C=C		*cis* olefin; RHC=CHR′
6.03–6.07	1658–1648		C=C		terminal olefin; $RR'C=CH_2$
6.06–6.17	1650–1620	s	N—H	def.	primary amide (solid): Amide II,
6.06–6.25	1650–1600	s	NO_2	asym. str.	$-O-NO_2$, nitrate
6.06–6.33	1650–1580	m–s	N—H	def.	NH_2; primary amine
6.06–6.45	1650–1550	w	N—H	def.	NHR; secondary amine
6.07–6.11	1648–1638		C=C		terminal olefin; $RHC=CH_2$
~6.15	~1625	s	C=C	str.	Ph-conjugated C=C
6.15–6.31	1625–1585	m	C=C	skeletal, in-plane	aromatic C=C
6.17–6.29	1620–1590	s	N—H	def.	primary amide (dil. soln.)
6.17–6.41	1620–1560	m–s	NH_2^+	def.	
6.21–6.49	1610–1540	vs	C—O	asym. str.	$-COO^-$, carboxylate
~6.25	~1600	s	C=C	str.	CO or C=C conjugated with C=C
~6.31	~1585	m	NH_3^+	asym. def.	amine salt
6.33–6.58	1580–1520	m	C=N (plus C=C)		pyrimidines
6.37–6.60	1570–1515	s	N—H	def.	secondary amide (solid): Amide II
6.45–6.62	1550–1510	s	N—H	def.	secondary amide (dil. soln.)
~6.67	~1500	var	C=C	skeletal, in-plane	aromatic C=C
6.67–6.80	1500–1470	s	C=S	str.	—N—C=S
6.67–7.69	1500–1300	m	NH_3^+	sym. def.	amine salt
~6.81	~1468	s	C—H	scissoring	alkane $-CH_2-$
~6.85	~1460	m	C—H	bend (asym.)	$-CH_3$

See footnotes at end of table.

TABLE 1. *Characteristic infrared bands shown by various groups*—Continued

Range		Intensity [a]	Group	Type of vibration [b]	Remarks
μm	cm^{-1}				
6.85–7.15	1460–1400	s	C—O	sym. str.	—COO^-, carboxylate
~6.87	~1455	s	C—H	scissoring	alicyclic —CH_2—
6.90–7.15	1450–1400	w	—N=N—	str.	azo
6.95–7.17	1440–1395	w	C—O	str. (plus OH def.)	carboxylic acid
6.95–7.41	1440–1350	s	S=O	str.	$(RO)_2SO_2$, sulfuric ester
6.95–7.55	1440–1325	m	C—C		aliphatic aldehyde
7.04–7.11	1420–1406	w	C—H	in-plane bend	C=CH_2
7.04–7.52	1420–1330	s	S=O	str.	$ROSO_2R'$, sulfonic ester
7.05–7.15	1418–1400	m	C—N	str.	primary amide
~7.09	~1410	w	C—N	str.	aliphatic amine
7.19–7.35	doublet, 1390–1360	m	C—H	bend (sym.)	*gem*-dimethyl
7.22–7.28	1385–1375	m	C—H	bend (sym.)	—CH_3
7.30–8.00	1370–1250		C—O	str.	lactone
~7.46	~1340	w	C—H	bend	alkane C—H
7.46–7.81	1340–1280	s	S=O	sym. str.	R_2SO_2, sulfone
7.46–8.48	1340–1180	w	N≡N	str.	azide
7.58–8.27	1320–1210	s	C—O	str.	carboxylic acid
7.64–8.00	1310–1250	s	C—O	str.	benzoic ester, phthalic ester
7.66–8.33	1305–1200	m	N—H	def.	secondary amide, Amide III
7.69–8.00	1300–1250	s	NO_2	sym. str.	—O—NO_2, nitrate
7.69–8.33	1300–1200	s	P=O	str.	phosphoric ester, free P=O
7.88–8.70	1270–1150	s	C—O	str.	—(O=)C—O—R in carboxylic esters
7.96–8.12	1256–1232	s	C—O	str.	CH_3COOR, acetic ester
~8.00	~1250		C—O	str.	methylene acetal
~8.00	~1250		C—O	str.	epoxide
~8.00	~1250	vs	Si—CH_3	sym. CH_3 def.	$Si(CH_3)_3$, trimethylsilyl
8.00–8.70	1250–1150	vs	P=O	str.	phosphoric ester, H-bonded P=O
8.10–8.25	1235–1212	s	C=S	str.	$(RO)_2C$=S, thioketone
8.13–8.70	1230–1150	s	S=O	str.	$(RO)_2SO_2$, sulfuric ester
8.16–8.51, 8.89–9.18, 9.35–10.00	1225–1175, 1125–1090, 1070–1000 (two)	w	C—H	in-plane bend	*p*-substituted phenyl
8.20–9.80	1220–1020	m	C—N	str.	aliphatic amine
8.33–8.73	1200–1145	s	S=O	str.	$ROSO_2R'$, sulfonic ester
8.33–9.62	1200–1040		C—O	str.	C—O—C—O—C, cyclic acetal (4–5 bands)
8.33–8.55	1200–1170	s	C—O	str.	propionic and higher esters
8.33–10.00	1200–1000	s	C—OH	str.	alcohols
8.44–8.51	1185–1175	s	C—O	str.	formic ester
8.51–8.59, 8.55–8.77	1175–1165 and 1170–1140	s	C—H	skeletal	$(CH_3)_2C<$, isopropyl
8.51–8.89, 9.01–9.35, 9.35–10.00	1175–1125, 1110–1070, 1070–1000	w	C—H	in-plane bend	unsubstituted phenyl
8.70–9.09	1150–1100	s	S=O	asym. str.	R_2SO_2, sulfone
8.70–9.09	1150–1100	s	C—O	str.	benzoic ester, phthalic ester
8.70–9.35	1150–1070	s	C—O—C	asym. str.	aliphatic ether
~8.93	~1120	s	C=S	str.	—NH—(C=S)—, thioamide
9.01–10.00	1110–1000	s	C—F	str.	monofluoro derivs.
9.18–9.71	1090–1030	vs	P—O—C		phosphoric ester
9.18–9.80	1090–1020	vs	Si—O	str.	Si—O—C, trimethylsilyl
9.45–9.50	1058–1053	s	C=S	str.	$(RS)_2C$=S, trithiocarbonate
9.52–9.80	1050–1020	s	S=O	str.	>S=O, sulfoxide
~9.62	~1040		C—O	str.	methylene acetal
9.95–10.10, 10.93–10.99	1005–990 and 915–910	vs	C—H	bend	C=C—H, vinyl
10.05–10.15, 10.99–11.05	995–985 and 910–905		C—H	out-of-plane bend	$RCH=CH_2$
10.20–10.36	980–965		C—H	out-of-plane bend	*trans* RHC=CHR′
10.31–10.64	970–940	broad	P—O—P		pyrophosphate
10.36–10.42, 10.58–10.64	965–960 and 945–940	s	C—H	bend	vinyl ether
10.42–10.75	960–930		N—O	str.	oxime

See footnotes at end of table.

TABLE 1. *Characteristic infrared bands shown by various groups*—Continued

Range		Intensity [a]	Group	Type of vibration [b]	Remarks
μm	cm^{-1}				
10.53–12.35	950–810		C—O	str.	epoxide
~10.55	~948	s	C—H	bend	vinyl ester
~10.81	~925		C—O	str.	methylene acetal
11.17–11.30	895–885		C—H	out-of-plane bend	$RR'C{=}CH_2$
~11.90	~840	vs	$Si{-}CH_3$	str.	$Si(CH_3)_3$, trimethylsilyl
11.90–12.66	840–790		C—H	out-of-plane bend	$RR'C{=}CHR''$
11.90–12.66	840–790	m	C—H	skeletal	$(CH_3)_2C<$, isopropyl
11.90–13.33	840–750		C—O	str.	epoxide
12.00–12.35	833–810	vs	C—H	out-of-plane bend	*p*-substituted phenyl
~12.50	~800	w	NH_3^+	rocking	amine salt
~12.50	~800	w	NH_2^+	rocking	
12.99–13.70, 14.08–14.49	770–730, 710–690	s	C—H	out-of-plane bend	unsubstituted phenyl
~13.25	~755	vs	$Si{-}CH_3$	str.	$Si(CH_3)_3$, trimethylsilyl
13.33–14.08	750–700	s	C—Cl	str.	monochloro derivs.
~13.89	~720	m(broad)	N—H	def.	secondary amide, bonded: Amide V
14.18–17.54	705–570	w	C—S	str.	thiol, sulfide
~14.49	~690		C—H	out-of-plane bend	*cis* RHC=CHR′
~15.39	~650	s	C—Br	str.	bromo derivs.
16.67–20.83	600–480	s	C—I	str.	iodo derivs.
18.19–22.22	550–450	vw	S—S	str.	disulfide

[a]Key: m, medium; s, strong; v, very; var, variable; w, weak.
[b]asym., asymmetrical; def., deformation; str., stretching; sym., symmetrical.

Description of a group vibration as A—B stretching or A—B—C bending is, at best, a first approximation. All of the bonds in a group are usually changing to some extent during a vibration. One bond may dominate, and it is then reasonable to describe the vibration as the motion of that bond, but this is by no means always justifiable. Thus, for the amide group vibrations, the stretching motions of C=O, C—N, and N—H and the corresponding bending motions are often highly mixed; consequently, the amide group vibrations are described as Amide I, II, III, and so on.

In the following discussion of some of the more important bands, all values for their positions are approximate unless a range is stated; even so, although frequencies generally fall within the limits indicated, they may, in special cases, lie beyond these ranges. Consequently, when the correlations are used, all other available evidence should also receive consideration. Also, in this discussion, the reference given is usually, but not necessarily, that for the first mention of the correlation for carbohydrates.

4.2.1. C—H Bands

All sugars and their derivatives possess the methylidyne (methine) grouping $-\overset{|}{\underset{|}{C}}-H$, characterized by a band near 3.45 μm (2900 cm^{-1})[1] assigned to C—H stretching. Hence, this band has no diagnostic value for these compounds.

Acetylenic compounds give a strong band for C—H stretching of ≡C—H at about 3.07 μm (3255 cm^{-1}); this occurs at 3.03 μm (3300 cm^{-1}) for 5-hexyne-D-*lyxo*-1,2,3,4-tetrol tetraacetate [23] and at 3.11 μm (3215 cm^{-1}) for 1,2:3,4-di-*O*-isopropylidene-6-heptyne-D-*gulo*-1,2,3,4,5-pentol [24]; the L-*manno* isomer of the latter shows the band at 3.06 μm (3268 cm^{-1}).

Other C—H stretching frequencies encountered with sugar derivatives are: olefinic $=CH_2$ doublet at 3.25 μm (3075 cm^{-1}) and 3.36 μm (2975 cm^{-1}); Ar—H at 3.28 μm (3050 cm^{-1}); olefinic $=\overset{|}{C}-H$ at 3.31 μm (3020 cm^{-1}); $-CH_2-$ doublet at 3.42 μm (2925 cm^{-1}) and 3.51 μm (2850 cm^{-1}); and *C*-methyl doublet at 3.38 μm (2960 cm^{-1}) and 3.49 μm (2865 cm^{-1}). Thus, a group of 28 cyclic acetals of various sugars all showed [4] a band at 3.32 to 3.37 μm (3010 to 2965 cm^{-1}). As regards *O*-methyl, all of 21 methyl aldopyranosides studied [12] showed a characteristic C—H stretching band at 3.47–3.52 μm (2882–2841 cm^{-1}), not shown by *C*-methyl or ethoxyl groups [25] that permits detection of the glycosidic methoxyl group.

Some deformation frequencies for C—H are: $-CH_2-$ at 6.89 μm (1450 cm^{-1}), and *C*-methyl

at 7.27 μm (1375 cm^{-1}). The *C*-methyls of the isopropyl group show bands at 7.25 and 7.30 μm (1380 and 1370 cm^{-1}) that are particularly useful for indicating the presence of the isopropylidene acetal structure.

Weak bands for C—H in-plane deformations of the unsubstituted phenyl group are found at 8.51 to 8.89 μm (1175 to 1125 cm^{-1}), 9.01 to 9.35 μm (1110 to 1070 cm^{-1}), and 9.35 to 10.00 μm (1070 to 1000 cm^{-1}); strong bands for C—H out-of-plane deformations occur at 12.99 to 13.70 μm (770 to 730 cm^{-1}) and 14.08 to 14.49 μm (710 to 690 cm^{-1}).

For substituted phenyl groups, the bands for C—H in-plane and out-of-plane deformation differ according to the position and degree of substitution. For the *p*-substituted phenyl group, most commonly encountered in sugar chemistry, weak bands (in-plane deformations) are found at 8.17 to 8.51 μm (1225 to 1175 cm^{-1}), 8.89 to 9.17 μm (1125 to 1090 cm^{-1}), and 9.35 to 10.00 μm (1070 to 1000 cm^{-1}), and a strong band (out-of-plane deformation) at 11.63 to 12.50 μm (860 to 800 cm^{-1}). Thus, the *p*-substituted phenyl group of *p*-toluenesulfonic esters of alditols [26] and sugars [27] shows a hydrogen out-of-plane deformation at 12.05 to 12.35 μm (830 to 810 cm^{-1}), not shown by methanesulfonates.

For the olefins, $CHR{=}CH_2$ shows a weak band at 7.04 to 7.09 μm (1420 to 1410 cm^{-1}), a band at 7.69 to 7.75 μm (1300 to 1290 cm^{-1}), a medium-strength band at 10.05 and 10.15 μm (995 to 985 cm^{-1}), and a strong band at 10.93 to 11.05 μm (915 to 905 cm^{-1}). A *cis* double bond shows a weak band at 7.04 to 7.14 μm (1420 to 1400 cm^{-1}) and a strong band at 13.70 to 15.04 μm (730 to 665 cm^{-1}); a *trans* double bond shows a weak band at 7.55 to 7.75 μm (1325 to 1290 cm^{-1}) and a strong band at 10.20 to 10.42 μm (980 to 960 cm^{-1}). For example, *trans*-3-hexene-D-*threo*-1,2,5,6-tetrol [28] shows bands at 7.55 and 10.25 μm (1325 and 976 cm^{-1}); its 1,2:5,6-di-*O*-isopropylidene derivative shows bands at 7.65 μm (1307 cm^{-1}) and 10.30 μm (971 cm^{-1}).

Whiffen et al. [29] have succeeded in identifying the C—H deformation vibrations at the anomeric carbon atom of various aldoses by replacing the hydrogen atom on C-1 with deuterium. For example, to prepare α-D-glucopyranose-*1-C-d*, they dissolved D-glucono-1,5-lactone in deuterium oxide, reduced the carbonyl group to —C(OD)— with sodium amalgam in deuterium oxide, and then converted the OD groups into OH groups by 3 times dissolving in water and evaporating; the C—D bond at C-1 remained unchanged. The spectrum of the α-D-glucopyranose-*1-C-d* was then compared with that of α-D-glucopyranose. Now, by theory, if ^1H is replaced by D (^2H), the ^1H deformation frequencies are approximately $\sqrt{2}$ times the corresponding deuterium frequencies (in cm^{-1}) if the deformation corresponds to a pure bending or stretching mode. They found C-1—H at 7.28 μm (1375 cm^{-1}) and C-1—D at 9.13 μm (1095 cm^{-1}) (frequency ratio 1.26); and C-1—H at 7.79 μm (1284 cm^{-1}) and C-1—D at 10.36 μm (965 cm^{-1}) (ratio 1.33), as compared to the theoretical ratio of 1.414. Similar assignments were made for the β anomer and for the two anomers of other sugars.

4.2.2. N—H Bands

In dilute solution in a nonpolar solvent, primary amines show two bands in the region of 2.86 to 3.03 μm (3500 to 3300 cm^{-1}) due to stretching vibrations of the NH_2 group. If hydrogen bonding occurs, or if the solid is examined, the range is shifted to 2.86 to 3.23 μm (3500 to 3100 cm^{-1}). Secondary amines in dilute solution show only one N—H stretching band, at 2.94 to 3.03 μm (3400 to 3300 cm^{-1}).

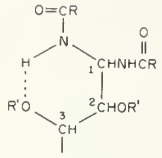
An N—H deformation frequency is shown by primary amines at 6.08 to 6.45 μm (1645 to 1550 cm^{-1}); thus, D-glucosylamine shows a band at 6.17 μm (1621 cm^{-1}), and 2-amino-2-deoxy-D-glucopyranose at 6.25 μm (1600 cm^{-1}) [3]. A band at 6.33 to 6.62 μm (1580 to 1510 cm^{-1}) is shown by —NH—.

The NH_2 deformation frequency of primary amides occurs at 6.06 to 6.17 μm (1650 to 1620 cm^{-1}) for the solid, and at 6.17 to 6.29 μm (1620 to 1590 cm^{-1}) for solutions; it is called the Amide II band. Secondary amides, having an NH group, show the Amide II band at 6.37 to 6.60 μm (1570 to 1515 cm^{-1}) for the solid, and at 6.45 to 6.62 μm (1550 to 1510 cm^{-1}) for solutions. Hydrogen-bonded secondary amides show an NH deformation mode near 13.89 μm (720 cm^{-1}), called the Amide V band.

The spectra of 16 1-acetamido derivatives of sugars [19] showed at least one band at 2.98 to 3.09 μm (3356 to 3236 cm^{-1}), attributed to N—H stretching; and, at 6.35 to 6.49 μm (1575 to 1541 cm^{-1}), the Amide II band. In a study of the spectra of 60 1-acylamido derivatives of aldofuranoid, aldopyranoid, and acyclic sugars [2], all of the compounds were secondary amides, and all of them showed at least one band at 2.89 to 3.10 μm (3460 to 3226 cm^{-1}) due to N—H stretching; in this region, completely esterified compounds could not be distinguished from those having free hydroxyl groups that would show O—H stretching in the same region. All of the compounds showed a band at 6.35 to 6.65 μm (1575 to 1504 cm^{-1}; Amide II).

The acyclic, 1,1-bis(acylamido)-1-deoxyalditols showed [2] two Amide II bands, suggesting that the two acylamido groups on C-1 of these compounds are not equivalent. They may have a hydrogen-bonded structure, possibly of the following type.

290-633 O - 68 - 2



where R is Me, Et, or Ph; and R′ is H, Ac, EtCO, or Bz.

4.2.3. O—H Bands

Compounds having a free hydroxyl group show a band for O—H stretching at 2.68 to 2.84 μm (3730 to 3520 cm^{-1}). The O—H bond is weakened if the hydroxyl group is hydrogen-bonded, and the band is broadened, with a shift to longer wavelength, 2.84 to 3.22 μm (3520 to 3100 cm^{-1}). The band for O—H deformation lies at 9.26 to 9.71 μm (1080 to 1030 cm^{-1}). For sugars, differentiation of primary from anomeric and secondary hydroxyl groups by OH frequencies is not feasible, because of frequency shifts caused by hydrogen bonding.

Infrared spectra may be used for the detection of hydrogen bonding, which may be between one molecule and another (intermolecular) or in one molecule (intramolecular). For compounds soluble in carbon tetrachloride, intermolecular hydrogen-bonding is negligible at concentrations below 0.005 *M*, and absorptions at *ca.* 2.79 μm (*ca.* 3585 cm^{-1}) and *ca.* 2.76 μm (*ca.* 3625 cm^{-1}) may be associated with bonded and free hydroxyl groups, respectively [5]. In this way, the extent of intramolecular hydrogen bonding may be determined [7, 30]. In pyranoid (and *m*- or *p*-dioxane) derivatives, a suitably located hydroxyl group can form a hydrogen bond with the ring oxygen-atom, as shown in figure 3. The spectra are consistent with the equilibria shown, assuming that the molecules exist preferentially in the chair

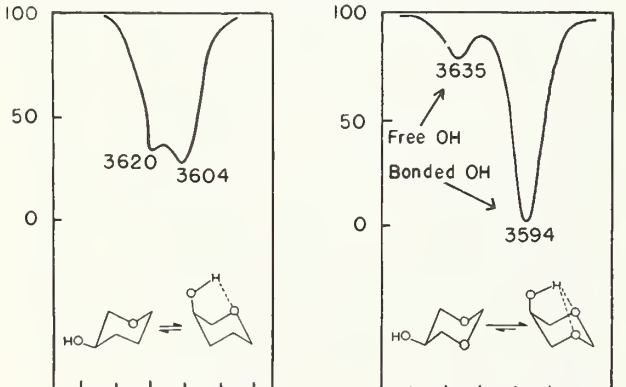
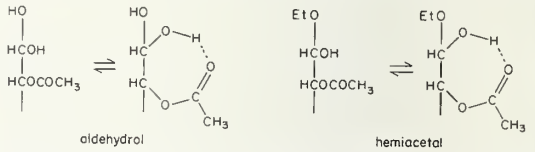


FIGURE 3. *Infrared spectra of tetrahydropyran-3-ol (A) and of 1,3-O-methyleneglycerol (B) in carbon tetrachloride; both solutions 0.005* M.

(From Ref. [7].)

conformations (as against non-chair conformations). For compounds that are insufficiently soluble in carbon tetrachloride, Åkermark [31] has suggested the use of *p*-dioxane, which disrupts intermolecular hydrogen-bonds but does not affect strong intramolecular hydrogen-bonds.

In solution, both penta-*O*-acetyl-*aldehydo*-D-galactose aldehydrol and the corresponding ethyl hemiacetal show [17] a band at 2.78 μm (3597 cm^{-1}) for free hydroxyl, and a band at 2.87 μm (3483 cm^{-1}) for hydrogen-bonded hydroxyl.



The OD bands in the spectra of fully *O*-deuterated sugars have been examined [32]. The OH band at 2.95 μm (3390 cm^{-1}) of α,β-D-glucose was shifted, by deuteration, to 4.05 μm (2469 cm^{-1}), a wavenumber ratio of 1.37, and other new bands appeared.

4.2.4. C≡C and C=C Bands

The C≡C stretching absorption is weak and has limited diagnostic value; it is not shown by symmetrically disubstituted acetylenes. A weak stretching band for H—C≡C—R lies at 4.65 to 4.76 μm (2150 to 2100 cm^{-1}); thus, 5-hexyne-D-*lyxo*-1,2,3,4-tetrol tetraacetate shows [23] a band at 4.65 μm (2150 cm^{-1}) and two 6-heptynepentol derivatives show [24] the band at 4.72 to 4.74 μm (2120 to 2110 cm^{-1}). For R—C≡C—R′, the band is at 4.42 to 4.57 μm (2260 to 2190 cm^{-1}).

Stretching frequencies for (phenyl) conjugated C=C bonds give a strong band at about 6.15 μm (1625 cm^{-1}); for CO or C=C conjugation, the band occurs at about 6.25 μm (1600 cm^{-1}). Bands for nonconjugated C=C bonds occur at 5.95 to 6.17 μm (1680 to 1620 cm^{-1}). For olefins, bands are found for a *cis* double bond in RCH=CHR′ at 6.02 to 6.05 μm (1662 to 1653 cm^{-1}), and for the *trans* form at 5.96 to 6.05 μm (1678 to 1653 cm^{-1}). For example, *trans*-3-hexene-D-*threo*-1,2,5,6-tetrol shows [28] a band at 6.05 μm (1653 cm^{-1}). A terminal, exocyclic double bond, as in $H_2C{=}CRR'$, shows a band at 6.03 to 6.07 μm (1658 to 1648 cm^{-1}), and for $H_2C{=}CHR$ at 6.07 to 6.11 μm (1648 to 1638 cm^{-1}).

The unsubstituted phenyl ring (C_6H_5) shows bands of medium, variable intensity for skeletal, in-plane, stretching vibrations of aryl C=C at 6.16 to 6.35 μm (1625 to 1575 cm^{-1}), 6.29 to 6.36 μm (1590 to 1575 cm^{-1}), 6.38 to 6.94 μm (1465 to 1440 cm^{-1}), and 6.56 to 6.78 μm (1525 to 1475 cm^{-1}). Thus, the phenyl (monosubstituted benzene) ring of the benzoyl group shows bands at 6.25 and 6.32 μm (1600 and 1584 cm^{-1}). For example, a group of 1-acylamido sugar derivatives having *N*-benzoyl or *O*-benzoyl groups, or both, showed [2] bands at 6.20 to 6.25 μm (1613 to 1600 cm^{-1}), 6.30 to 6.38 μm (1587 to 1567 cm^{-1}), and

6.64 to 6.77 μm (1506 to 1477 cm^{-1}); and the *p*-substituted phenyl ring of *p*-toluenesulfonic esters of alditols [26] and sugars [27] shows an aryl C=C band at 6.23 to 6.25 μm (1605 to 1600 cm^{-1}) which differentiates them from methanesulfonates.

4.2.5 C≡N, C=N, and C—N Bands

The stretching band for C≡N lies in the range of 4.17 to 4.76 μm (2400 to 2100 cm^{-1}); thus, for R—C≡N, it is found at 4.43 to 4.47 μm (2260 to 2240 cm^{-1}), and, for conjugated R—C≡N, at 4.47 to 4.52 μm (2240 to 2215 cm^{-1}). For isocyanides, R—N≡C, the band is at 4.55 to 4.76 μm (2200 to 2100 cm^{-1}). For —S—C≡N, the band is found at *ca.* 4.63 μm (*ca.* 2160 cm^{-1}).

Compounds containing C=N— show a band at 6.02 to 6.21 μm (1660 to 1610 cm^{-1}) that has been used in determining whether such compounds as *N*-substituted glycosylamines are cyclic or acyclic (see p. 18). However, the compound examined must be scrupulously dry, as moisture shows a band at 6.06 to 6.25 μm (1650 to 1600 cm^{-1}). Moreover, hydrates cannot be employed, as water of crystallization shows a band at 6.06 to 6.10 μm (1650 to 1640 cm^{-1}).

For —N=C=S (isothiocyanate) and —N=C=N— (carbodiimides), a strong band is shown at *ca.* 4.76 μm (*ca.* 2100 cm^{-1}).

Aliphatic amines show a medium-intensity band for C—N stretching at 8.20 to 9.80 μm (1220 to 1020 cm^{-1}) and a weak band at about 7.90 μm (1410 cm^{-1}). Nitro compounds show a band (medium intensity) for C—N stretching at 10.87 to 11.76 μm (920 to 850 cm^{-1}), and primary amides at 7.05 to 7.15 μm (1418 to 1400 cm^{-1}). Of less diagnostic value are a C—N band at 7.30 to 7.63 μm (1370 to 1310 cm^{-1}) for the *N*-methyl group, and the Ph—N stretching band, observed [33] at 8.70 to 8.84 μm (1149 to 1131 cm^{-1}) or [34] 8.62 to 8.85 μm (1160 to 1130 cm^{-1}), for phenylhydrazones and phenylazo derivatives.

4.2.6. C=O Bands

(*a*) *Aldehydes and Ketones.*—The C=O stretching frequency for the carbonyl group of aldehydes and ketones lies at 5.78 to 6.00 μm (1730 to 1665 cm^{-1}). Thus, for the acyclic form of certain aldoses and ketoses (in a lyophilizate of the mutarotational equilibrium mixture), an extremely weak band is detectable [13] at 5.82 μm (1718 cm^{-1}). Kuhn [14] attributed a band at 6.2 μm (1613 cm^{-1}) shown by periodate-oxidized methyl α-D-glucopyranoside to aldehydic carbonyl. Periodate-oxidized cellulose shows only a very weak band [35], and has been shown [36] to exist mainly as the hemialdal —CH—(OH)—O—CH(OH)—, formed by hydration of two aldehyde groups per oxidized residue.

If the bands given by two different kinds of groups lie in close proximity in the spectrum (see table 1), the bands may be separate, but often one appears as a shoulder on the other, or one may completely obscure the other. For example, a number of anhydrous, monomeric, *aldehydo* sugar acetates show no strong band [17] for the aldehyde carbonyl group, presumably because it is obscured by the acetate carbonyl band. As a corollary, in the absence of other information, the CHO band could be mistaken for OAc or OBz. If such interference is absent, *aldehydo* and *keto* sugars show the C=O band; for example, 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose shows [37] a band at 5.8 μm (1724 cm^{-1}).

(*b*) *Un-ionized Carboxylic Acids.*—The C=O stretching frequency appears at 5.76 μm (1736 cm^{-1}) for —C(=O)OH of un-ionized carboxylic acids [38, 39], including alginic acid, chrondroitin sulfate, hyaluronic acid, and the pneumococcal polysaccharides.

(*c*) *Lactones.*—In 1958, Barker et al. [40] found that 22 out of 24 aldono-1,4-lactones showed a band at 5.59 to 5.67 μm (1790 to 1765 cm^{-1}), and all of 11 aldono-1,5-lactones showed a band at 5.68 to 5.79 μm (1760 to 1726 cm^{-1}). Consequently, if the spectrum shows a strong band at 5.60 μm (1785 cm^{-1}), there is a strong possibility that the aldonolactone is 1,4 and if it shows a band at 5.78 μm (1730 cm^{-1}), there is a possibility that it is 1,5. However, if it shows a band at 5.65 to 5.70 μm (1770 to 1775 cm^{-1}), some other method for distinguishing between the two should be used. The 6,3-lactones of 1,2-*O*-isopropylidene-α-D-gluco- and -β-L-ido-furanuronic acid show [4] C=O stretching [41] at 5.59 to 5.67 μm (1790 to 1765 cm^{-1}).

(*d*) *Acetates and Other Esters.*—The C=O stretching vibration of the *O*-acetyl group gives rise to strong absorption at 5.72 to 5.80 μm (1748 to 1724 cm^{-1}); thus, the octaacetates of α-cellobiose, α-gentiobiose, and β-maltose show [42] a strong band at 5.79 μm (1727 cm^{-1}), 5.72 μm (1748 cm^{-1}), and 5.76 μm (1736 cm^{-1}), respectively. Similarly, six acetates of cyclic acetals of sugars showed [4] a band at 5.72 to 5.75 μm (1748 to 1739 cm^{-1}); all of 24 acetylated aldopyranosides showed [18] at least one band in the region of 5.67 to 5.76 μm (1764 to 1736 cm^{-1}); all of 8 reducing, pyranose acetates showed [19] a band at 5.71 to 5.76 μm (1751 to 1736 cm^{-1}); all of 20 fully acetylated pyranoses [20] showed a band at 5.69 to 5.74 μm (1757 to 1742 cm^{-1}); and, for 14 acetates (and a tetrapropionate) of 1-acylamido derivatives of sugars, all showed [2] a band at 5.68 to 5.74 μm (1761 to 1742 cm^{-1}), except for *N*-acetyl-2,3,4-tri-*O*-acetyl-β-D-ribosylamine, showing [43] a band at 5.82 μm (1718 cm^{-1}). Benzoates of the same group of 1-acylamido derivatives showed [2] a band at 5.73 to 5.79 μm (1745 to 1727 cm^{-1}), except for 1,1-bis(benzamido)-6-*O*-benzoyl-1-deoxy-D-glucitol, showing a band at 5.89 μm (1698 cm^{-1}). Mixed esters (acetate-benzoates) showed two bands in this region.

The five-membered, cyclic carbonate group in sugar carbonates shows an enhanced C=O stretching frequency as compared with the mixed-ester carbonates of sugars, average values lying at 5.49 μm (1820 cm^{-1}) and 5.68 μm (1760 cm^{-1}),

respectively [44]. If the cyclic carbonate is *trans*-fused in sugar derivatives, a strong C=O stretching band is shown [45] at 5.43 μm (1842 cm^{-1}); the band is not shown by *cis*-fused carbonates.

(*e*) *Primary Amides.*—The C=O stretching frequency for —C(=O)NH_2 lies near 6.06 μm (1650 cm^{-1}) for solids, and near 5.92 μm (1690 cm^{-1}) for dilute solutions. It is known as the Amide I band, and is also shown by secondary and tertiary amides. Three glycopyranuronamide derivatives showed [19] this band at 6.00 to 6.02 μm (1667 to 1661 cm^{-1}).

(*f*) N-*Acetyl and* S-*Acetyl.*—The Amide I band for the monosubstituted amide group, as in —NH—(C=O)—CH_3, occurs at *ca.* 6.04 μm (1655 cm^{-1}) for solids, and at 5.88 to 5.99 μm (1700 to 1670 cm^{-1}) for dilute solutions. Thus, the anomers of 2-acetamido-2-deoxy-D-glucopyranose and their tetraacetates show [46] the band at 5.97 to 6.19 μm (1675 to 1616 cm^{-1}). For all of 16 1-acetamido derivatives of sugars, the band is shown [19] at 5.85 to 6.02 μm (1709 to 1661 cm^{-1}). Hydrates showed bands at 6.01 to 6.09 μm (1664 to 1642 cm^{-1}) that overlapped, somewhat obscured, or were obscured by, Amide I bands in the same region. Of 60 1-acylamido derivatives of sugars, all showed [2] a band at 5.95 to 6.15 μm (1681 to 1626 cm^{-1}). The Amide I band occurs near 6.07 μm (1648 cm^{-1}) for such polysaccharides as chitin [47], but at 6.18 μm (1618 cm^{-1}) for 2-acetamido-2-deoxy-α-D-glucopyranose, and at 6.01 μm (1665 cm^{-1}) for its tetraacetate, probably because of differences in the hydrogen bonding between the C=O group and OH and NH groups [3]. Because an ionized carboxyl group will absorb in this region, the spectra of such polysaccharides as chrondroitin sulfate should be recorded for films cast from an acid solution.

The carbonyl group in the *S*-acetyl group, —S—(C=O)—CH_3, shows [48] a band near 5.95 μm (1680 cm^{-1}). Thus, this group can be distinguished from the *O*-acetyl group, absorbing near 5.75 μm (1740 cm^{-1}) and the *N*-acetyl group, absorbing near 6.10 μm (1640 cm^{-1}).

4.2.7. C—O Bands

(*a*) *Esters.*—Strong bands for the C—O stretching vibrations are shown by esters; for example, by acetates at 8.00 to 8.13 μm (1250 to 1230 cm^{-1}), formates at 8.33 to 8.48 μm (1200 to 1180 cm^{-1}), and propionates at 8.33 to 8.55 μm (1200 to 1170 cm^{-1}). Esters of aromatic acids shows two strong bands for C—O stretching, at 7.69 to 8.00 μm (1300 to 1250 cm^{-1}) and 8.70 to 9.09 μm (1150 to 1100 cm^{-1}).

(*b*) *Carboxylate Ion.*—Salts of carboxylic acids, such as the lithium and barium salts of 1,2-*O*-isopropylidene-α-D-glucofuranuronic acid, show [4] a carbon—oxygen stretching band (strong) at 6.11 to 6.25 μm (1637 to 1600 cm^{-1}) that distinguishes carboxylate anions from the C=O stretching band of esters, and a band (medium strength) at 7.04 to 7.69 μm (1420 to 1300 cm^{-1}).

4.2.8. N≡N, N=N, and NO_2 Bands

The N≡N stretching vibration of azides gives a strong band at 4.63 to 4.72 μm (2160 to 2120 cm^{-1}) and a weak band at 7.46 to 8.48 μm (1340 to 1180 cm^{-1}). The N=N group in aromatic diazo compounds gives bands at 6.31 to 6.37 μm (1585 to 1570 cm^{-1}) and at 7.04 to 7.24 μm (1420 to 1381 cm^{-1}). According to Bassignana and Cogrossi [34], the bands lie at 6.32 to 6.42 μm (1582 to 1558 cm^{-1}) and 6.95 to 7.25 μm (1439 to 1379 cm^{-1}).

Nitric esters of sugars show [27] strong bands for asymmetric NO_2 stretching at 6.00 to 6.20 μm (1667 to 1613 cm^{-1}) and for symmetric NO_2 stretching at 7.78 to 7.89 μm (1285 to 1267 cm^{-1}); a broad band (for O—NO_2 stretching) at 11.48 to 12.08 μm (871 to 828 cm^{-1}) is useful only for confirmation as it occurs in a region that contains bands (Types 2a, 2c, and C) for sugars and the C—H out-of-plane deformation of the *p*-substituted phenyl group.

4.2.9. S=O, —SO_2—, and C=S Bands

Esters of sulfuric acid, such as the 6-sulfates of D-glucose, D-galactose, and 2-acetamido-2-deoxy-D-glucose, show [49] an intense band at 8.07 μm (1240 cm^{-1}), due to S—O stretching vibrations. The position of a band at 11.76 to 12.19 μm (850 to 820 cm^{-1}) for the C—O—S frequency of the sulfate group has been correlated with its attachment (primary or secondary) and with the axial or equatorial disposition if secondary (see page 16).

Sulfones show strong bands at 7.38 to 7.64 μm (1355 to 1310 cm^{-1}) and 8.62 to 9.01 μm (1160 to 1110 cm^{-1}) for S=O stretching; thus, the monosulfone obtained by oxidizing penta-*O*-acetyl-*aldehydo*-D-glucose dibenzyl dithioacetal shows a band at 7.66 μm (1305 cm^{-1}) [22].

p-Toluenesulfonic esters of alditols [26] show bands at 7.3 to 7.4 μm (1370 to 1350 cm^{-1}) and at 8.4 to 8.5 μm (1190 to 1175 cm^{-1}) for the asymmetrical and symmetrical stretching modes of the —SO_2— group [50, 51]. Sulfonic esters of sugars usually show two bands in each region [27]. Bands for C—O—S at 11.8 to 11.9 μm (848 to 840 cm^{-1}) and 11.2 to 11.4 μm (893 to 877 cm^{-1}) have been correlated with the axial or equatorial disposition of the sulfonic ester group (see page 16).

The C=S group of thionocarbonates shows [52] bands at 7.52 μm (1330 cm^{-1}) and at 7.65 μm (1307 cm^{-1}); a band at 8.40 μm (1190 cm^{-1}) is also found [51].

Dimethylthiocarbamates of sugars show, for OC(=S)NMe_2, a strong band [53] at 6.5 to 6.6 μm (1540 to 1515 cm^{-1}). *N,N*-Dimethyldithiocarbamates show, for —SC(=S)NMe_2, a strong band at 6.71 to 6.80 μm (1490 to 1470 cm^{-1}).

4.2.10. Miscellaneous Bands

The following bands are useful. (1) *Polystyrene* (for calibration): 3.51 μm (2851 cm^{-1}), 6.24 μm (1602 cm^{-1}), and 11.03 μm (907 cm^{-1}). (2) *Nujol:* 3.43 μm (2918 cm^{-1}), 3.50 μm (2861 cm^{-1}), 6.86 μm (1458 cm^{-1}), and 7.26 μm (1378 cm^{-1}) [and a weak band at 13.89 μm (720 cm^{-1})]. (3) *Water* as moisture: 2.92 μm (3430 cm^{-1}) and 6.06–6.25 μm (1650 to 1600 cm^{-1}).

Spurious bands may be introduced by a variety of causes, including silicone grease used on stopcocks, polyethylene powder from laboratory ware, and phthalic anhydride from the plasticizer in plastic tubing. About 35 spurious bands have been listed [54].

4.3. Correlations for the Fingerprint Region and Beyond

4.3.1. The Fingerprint Region

Whereas the spectra of structurally similar compounds may be quite similar in the range of 2 to 7 μm (5000 to 1430 cm^{-1}), significant spectral differences are found in the fingerprint region from 7 to 11 μm (1430 to 910 cm^{-1}), because here the bands are due both to certain stretching vibrations and bending vibrations. As a result, small differences in structure appear as large spectral effects. Consequently, the region is valuable for identification of a compound, and for differentiating between isomers, including anomers.

On the other hand, the fingerprint region is often less useful for recognizing the presence of particular organic groups than the region below 7 μm (above 1430 cm^{-1}), where the presence or absence of bands may give valuable, reliable evidence for characteristic groups. For example, the characteristic group-frequencies for α-(D or L)-glucopyranose are essentially the same as those for β-(D or L)-glucopyranose, and hence their spectra below 7 μm (above 1430 cm^{-1}) are similar; but, for crystals in which the molecules have the favored chair conformation, the interactions of the hydroxyl group at C-1 with the ring-oxygen atom of a neighboring molecule can be expected to be different for the axially attached group of the α-(D or L) anomer and the equatorially attached group of the β-(D or L) anomer, and therefore their spectra in the fingerprint region can be expected to differ. In the hydrogen-bonded structure proposed [55] for crystalline α-D-glucopyranose, the bonding between the C-1 hydroxyl group of one molecule and the ring oxygen atom of a neighbor would be different from that for the crystalline β-D anomer. Analysis of such differences by a combination of x-ray crystal-structure analysis, broad-line nuclear magnetic resonance spectroscopy, and infrared spectroscopy should eventually lead to improved interpretation of the bands in the fingerprint region and beyond, but this goal has not yet been reached.

4.3.2. Correlations for 10 to 15 μm (1000 to 667 cm^{-1})

(*a*) *Correlations for Certain Aldopyranose Derivatives.*—In a part of the fingerprint range, namely, 10.42 to 13.70 μm (960 to 730 cm^{-1}), Barker and co-workers [56–58] have sought infrared bands characteristic of several aldopyranoses and their derivatives. In the first of these articles, they identified [56], for D-glucopyranose derivatives, three principal sets of bands, given in table 2. These were: for α anomers, type 1a, 917±13 cm^{-1}; type 2a, 844±8 cm^{-1}; and type 3a, 766±10 cm^{-1}; and for β anomers, type 1b, 920±5 cm^{-1}; type 2b, 891±7 cm^{-1}; and type 3b, 774±9 cm^{-1}.

If the bands are to have diagnostic value for (D or L)-glucopyranose derivatives, α anomers should not show type 2b absorption, and β anomers should not show type 2a absorption. However, they found [56] that (a) some α anomers exhibit type 1 absorption in the range of type 2b bands, and (b) some β anomers show "weak peaks of type 2a" which they believed were due to traces of the α anomers. They found that the type 2a band can be used with considerable con-

TABLE 2. *Positions (mean values) of various types of bands for D-glucopyranose derivatives [56]*

Linkage	Type 1		Type 2a		Type 2b		Type 3	
α **Anomeric**	μm	cm^{-1}	μm	cm^{-1}	μm	cm^{-1}	μm	cm^{-1}
monosaccharides	10.93	915	11.81	847			13.04	767
	11.11	900	11.88	842			13.32	751
higher saccharides	10.75	930	11.86	843			13.14	761
	10.90	917	11.92	839			13.02	768
β **Anomeric**								
monosaccharides	10.94	914			11.16	896	—	—
	[a]10.89	[a]918			11.22	891	[b]12.95	[b]772
higher saccharides	10.86	921			11.24	890	[c]12.92	[c]774

[a] Six of ten compounds did not show this band. [b] Eleven of sixteen compounds did not show this band. [c] Five of sixteen compounds did not show this band.

TABLE 3. *Infrared bands (mean values) shown by five* (D *or* L)*-aldopyranoses and their derivatives* [*56, 57*]

Type of band	Xylose		Arabinose		Glucose		Mannose		Galactose	
	μm	cm^{-1}	μm	cm^{-1}	μm	cm^{-1}	μm	cm^{-1}	μm	cm^{-1}
	Both anomers									
1	?	?	?	?	10.90	917	?	?	?	?
2c	—	—	—	—	—	—	11.42	876	11.48	871
3			13.11	763	[a] 12.99	[a] 770	[a] 12.64	[a] 791	[a] 13.30	[a] 752
					[a] 13.28	[a] 753				
	α anomers only									
2a	—	—	—	—	[a] 11.85	[a] 844	[a] 12.00	[a] 833	[a] 12.12	[a] 825
3	13.35	749			[a] 11.86	[a] 843				
	β anomers only									
2a	—	—	11.86	843						
			11.82	845						
2b					[b] 11.22	[b] 891	[c] 11.20	[c] 893	[c] 11.17	[c] 895
					[b] 11.24	[b] 890				

[a] Many derivatives containing a benzene ring absorb here. [b] Must be confirmed by absence of absorption at *ca.* 11.85 μm (*ca.* 844 cm^{-1}). [c] Bands for other types of vibration also occur here.

fidence for diagnosing the α anomeric form, particularly in polymers of glucopyranose. The type 2b band was not found useful for diagnosing the β anomeric form, but the *absence* of the type 2a band was considered very useful for diagnosing the β anomeric form. They regarded the bands of types 1 and 3 as only useful for determining points of linkage in polymers of α-glucopyranose.

When the infrared spectra of additional glucopyranose derivatives were reported in their next paper [57], slightly different positions were found for bands of type 2a and type 3 (see table 3). As before, some of the α anomers were found to show type 1 absorption in the range of type 2b bands. Also, they pointed out that derivatives containing a phenyl ring may show absorption in the region of the type 2a band, and the acetates absorb in the region of the type 2b band. Their results [57] for bands characteristic of four other aldopyranoses and their derivatives are also summarized in table 3. With manno- and galactopyranose derivatives, the type 2a band can be used for diagnosing α anomers; absence of the type 2a band is useful for diagnosing the β anomeric form. A band at 11.30 to 11.53 μm (876 ± 9 cm^{-1}), designated type 2c, was found characteristic [57] of mannopyranose derivatives; and a band of type 2c, at 11.39 to 11.57 μm (871 ± 7 cm^{-1}), was considered characteristic of galactopyranose derivatives. The mean frequency for a given type of absorption may change with the group-configuration; thus, the mean for type 3 absorption is at 12.64 μm (791 cm^{-1}) for the *manno* configuration, but at 13.30 μm (752 cm^{-1}) for the *gluco* and *galacto* configurations.

In addition, Barker and co-workers [58] found that 2- and 3-deoxy derivatives of gluco-, manno-, and galacto-pyranose show absorption at 11.51 to 11.56 μm (869 to 865 cm^{-1}); seven 6-deoxy derivatives of mannopyranose or galactopyranose show a band near 10.34 μm (967 cm^{-1}).

Application of these correlations [56–58] has proved useful [3] in the study of many related compounds, including oligo- and poly-saccharides. Assignments suggested [3, 56–58] for the bands are given in table 4. It should be noted, however, that, in the range of 10 to 15 μm (1000 to 667 cm^{-1}), methyl β-D-xylopyranoside shows only three bands [12], namely, at 10.25 μm (976 cm^{-1}), 10.38 μm (963 cm^{-1}), and 11.14 μm (898 cm^{-1}); indeed, β-(D or L)-xylopyranose derivatives are not characterizable by any of the bands listed in table 3. This example shows that the bands listed in tables 3 and 4 cannot be regarded as characteristic of the pyranoid ring, *per se*, of aldopyranoid derivatives.

(b) *Correlations for Furanoid and Pyranoid Forms of Aldose and Ketose Derivatives.*—For aldo- and keto-furanose derivatives, Barker and Stephens [59] noted absorption bands at the following mean values: type A, at 10.82 μm (924 cm^{-1}); and type D, at 12.52 μm (799 cm^{-1}). Type A absorption could not be distinguished from types 1 or 2b of aldopyranoses, and therefore has no diagnostic value in differentiating between furanoid and pyranoid aldoses. In addition, most of the furanoid compounds also showed type B absorption at 11.38 μm (879 cm^{-1}) and type C absorption at 11.66 μm (858 cm^{-1}). It has been found [2, 4, 19] that these correlations are, in most instances, restricted to the compounds they studied, and cannot be extended to have a wider diagnostic applicability to related compounds.

In 1962, the infrared spectra of most of the readily available, unsubstituted aldo- and keto-pentoses and aldo- and keto-hexoses were pub-

Table 4. *Bands possibly characteristic of various features of some aldopyranose derivatives*

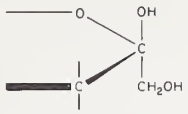
Type of band	Structural feature	Bands [a]		References
		μm	cm^{-1}	
	Terminal *C*-methyl-group rocking [b]	10.34	967	[58]
1	Antisymmetrical ring-vibration [c]	10.90	917	[56]
2b	Anomeric C—H axial bond	11.22	891	[56]
2c	Equatorial C—H deformation (other than anomeric C—H)	11.36	880	[57]
	Ring-methylene rocking vibration (if not adjacent to the ring-oxygen atom)	11.53	867	[58]
2a	Anomeric C—H equatorial bond	11.85	844	[56]
3	Symmetrical ring-breathing vibration	12.99	770	[56]

[a] Mean value. [b] This band may not have diagnostic value. [c] For glucopyranose derivatives.

lished [13]. In 1964, Verstraeten [60] made a study of these spectra, together with those of some additional 2-ketoses, and obtained evidence that most of the common sugars having a cyclic structure, and their derivatives, display type 1 absorption at a mean value of 10.76 μm (929 cm^{-1}). Hence, the type 1 (type A) band has no diagnostic value for distinguishing between aldoses and ketoses, and between glycofuranoses and glycopyranoses. Moreover, as the type 1 band is shown [2] by acyclic 1-acylamido derivatives of sugars, it has no diagnostic value for distinguishing between cyclic and acyclic forms of such compounds, either.

The same author [60] observed that some ketopyranoses, as well as aldopyranoses, show a type 3 band at 12.80 μm (781 cm^{-1}). Hence, this band, too, has limited diagnostic value. He concluded that type 3 absorption is shown provided that two conditions are met: (a) the sugar must have a pyranoid ring, and (b) this pyranoid form must assume a conformation having at least one axial hydroxyl group. If the number of axial hydroxyl groups is increased (thereby decreasing the conformational stability), type 3 absorption becomes manifest. For example, β-(D or L)-xylopyranose, which shows no type 3 absorption, is devoid of axial hydroxyl groups, whereas the α anomer in the favored conformation, which has an axial hydroxyl group at C-1 shows absorption at 13.16 μm (760 cm^{-1}).

It was found [60] that 2-ketoses display "type I" bands at 11.44 μm (874 cm^{-1}) and "type IIA" bands at 12.24 μm (817 cm^{-1}), regardless of whether the 2-ketoses are pyranose or furanose. These bands were ascribed to the presence of the following structural feature:



and were tentatively assigned to a skeletal vibration. However, six aldoses also show these bands. The type I band, which appears to be the same as Barker's type B band for aldo- and keto-furanoses at 11.38 μm (879 cm^{-1}), has [2] no diagnostic value for 60 aldofuranoid, aldopyranoid, and acyclic 1-acylamido derivatives. The type IIA band lies in about the same range as Barker's type D band for aldo- and keto-furanose derivatives, which is at 12.52 μm (799 cm^{-1}). If the hydroxyl groups of a 2-ketofuranose are substituted, or if C-2 of the 2-ketofuranose is joined to a pyranoid or furanoid structure, a type IIB band appears at 11.99 μm (834 cm^{-1}), in addition to, or instead of, the type IIA band.

Verstraeten [60] found that only furanoses give "type 2" absorption at 11.76 μm (850 cm^{-1}). He stated that his type 2 absorption is the same as the type C absorption of Barker and Stephens [59], and, to avoid confusion, it should be referred to as the latter. The type C band is given by both aldo- and keto-furanoses, and therefore cannot be used for distinguishing between them.

It has been found [2] that, if an *N*-acetyl group (but no ester group) is present, the bands of types C, 3, IIA, and IIB may have diagnostic value; also, if an *N*-benzoyl group (but no ester group) is present, the bands of types 3, IIA, and IIB may have diagnostic value. For *N*-acetyl-*O*-acetyl derivatives of sugars, the bands of types IIA and IIB may differentiate between ketoses and nonketoses, but not between cyclic and acyclic compounds.

4.4. Conformational Studies

In studying the conformations of sugar derivatives, the most direct information is obtained by nuclear magnetic resonance spectroscopy. However, the empirical correlation of infrared spectra has been used [12] to give conformational information. Suppose that the spectra of the α and β anomers of the methyl pyranosides of the 4 aldopentoses and 8 aldohexoses were to be recorded. This would provide 24 spectra of closely related compounds. Each compound has C—H, C—OH, C—OCH_3, and a pyranoid ring, and yet the spectrum of each is unique because the precise positions of the various bands change from one compound to another, depending on interactions arising from configuration and conformation and on the presence or absence of the hydroxymethyl group.

As an example, the spectra of the α and β anomers of methyl D-xylopyranoside and methyl L-arabinopyranoside were studied [12]. All bands shown in common by the four glycosides were ignored. All bands then shown in common by the two xylosides were regarded as characteristic of the *xylo* configuration and were ignored; similarly, all bands shown in common by the two arabinosides were ignored. This left a set of bands differentiating between the anomers of the xylosides, on the one hand, and between the arabinoside anomers, on the other (see table 5). This indicated a similarity between the β-D-xylopyranoside and the α-L-arabinopyranoside. Since the conformation of methyl β-D-xylopyranoside has been shown [61] by x-ray studies to be that depicted in fig. 4, the conformational correlations are as indicated. These formulas are in agreement with the conformations predicted by considerations of interaction energies.

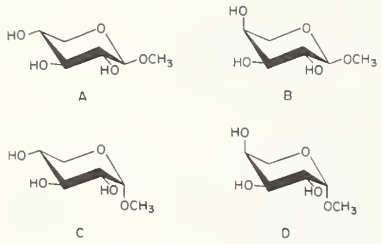


FIGURE 4. *The structures of methyl β-D-xylopyranoside-CA (A) and methyl α-L-arabinopyranoside-CE (B) compared with those of methyl α-D-xylopyranoside-CA (C) and methyl β-L-arabinopyranoside-CE (D).*

This correlation is purely empirical, but the same kind of comparison has been made for other pairs of anomers of (a) methyl aldopyranosides [12], (b) acetylated methyl aldopyranosides [18], and (c) fully acetylated aldopyranoses [20]. In every instance, the empirical observations made on the infrared spectra agreed with the predicted conformations. With those sugar derivatives for which one chair conformation is not predicted to be strongly favored over the other, the resulting data did not fit in the correlations. Examples of the latter are: methyl α- and β-D-lyxopyranoside and their triacetates, methyl α-D-gulopyranoside and its tetraacetate, and penta-*O*-acetyl-α-D-gulopyranose.

For a group of fully acetylated monosaccharides, those having an axial OAc at C-1 showed [17] a band, possibly for a C—O stretching vibration, at 8.59 to 8.67 μm (1174 to 1153 cm^{-1}); if the group was equatorial, a band was shown at 8.87 μm (1127 cm^{-1}). For each region, the other anomer showed the absorption only weakly or not at all. The results with compounds having the *gulo*, *ido*, and *talo* configurations indicated that they exist in the CE conformation, or as a mixture of the chair conformations.

For acetylated methyl glycosides [17], those having an axial OMe at C-1 showed bands at 8.31 to 8.35 μm (1203 to 1198 cm^{-1}) and at 8.75 to 8.85 μm (1143 to 1130 cm^{-1}), but those having the group equatorial showed no absorption in either region.

Because polysulfated hyaluronic acid, which has equatorial sulfate groups only, shows a band at 12.19 μm (820 cm^{-1}), Orr [39] concluded that the sulfate group of chondroitin sulfate C, showing a band at 12.12 μm (825 cm^{-1}), is equatorially attached, and that that of chondroitin sulfate A, giving a band at 11.70 μm (855 cm^{-1}), is axially attached. He ascribed the bands to the C—O—S vibration. It was then found [62] that the equatorial sulfate group in D-glucose 3-sulfate gives a band at 12.02 μm (832 cm^{-1}), and that a band at 12.19 μm (820 cm^{-1}) is shown by the 6-sulfates of D-galactose, D-glucose, and 2-acetamido-2-deoxy-D-glucose, in which the ester group is on the equatorial, primary hydroxyl group. Hence, chondroitin sulfate C (and D) probably has an equatorial sulfate group on C-6, and chondroitin sulfate A (and B) has an axial sulfate group on C-4 of the 2-acetamido-2-deoxy-D-galactose residues. Chondroitin polysulfate has sulfate groups at both C-4 and C-6.

Similarly, λ-carrageenan shows [63] a broad band at 11.62 to 12.35 μm (860 to 810 cm^{-1}), with a maximum at 12.09 μm (827 cm^{-1}) compatible with the presence of residues of D-galactose 2,6-disulfate (diequatorial) and D-galactose 4-sulfate (axial).

A strong band at 11.8 to 11.9 μm (848 to 840 cm^{-1}) and a weak one at 11.2 to 11.4 μm (893 to 877 cm^{-1}) are shown by sulfonic esters of pyranoid sugars, and have been attributed [50] to the C—O—S vibration of an equatorial and an axial sulfonic ester group, respectively, on a pyranoid ring.

TABLE 5. *Anomer-differentiating bands (cm^{-1}) shown by four methyl pyranosides [12]*

D-xylo		L-arabino	
β	α	α	β
3448		3460	
1385		1395	
1295		1295	
1218		1227	
1060		1058	
976		973	
645		646	
473		487	
	3333		3322
	2710		2695
	741		744
	437		433

5. Examples of Use of Infrared Spectra

In addition to those already mentioned, the following are some examples of the uses of infrared spectra.

5.1. Qualitative

Infrared spectra may be employed in following the course of a reaction. For example, if a compound requires several methylations to give a completely *O*-methylated product, the extent of methylation may be determined by observing the disappearance of OH absorption from the infrared spectrum, so that quantitative determination for methoxyl need be made only on the final product.

The elementary approach has been applied [13] in studying the mutarotation of sugars. For a number of monosaccharides, an aqueous solution of one crystalline anomer was kept until mutarotation was complete; the solution was then lyophilized, and the spectrum of the lyophilizate was recorded and compared with those of the two crystalline anomers. For D-glucose, L-rhamnose, and D-mannose, all of the bands in the spectrum of the equilibrium mixture that are not shown by the α-pyranose anomer are either (a) shown by the β-pyranose anomer or (b) could be due to overlapping and summation of closely situated bands of the two anomers, indicating that the equilibrium mixture consists of the anomers of the pyranose form; this conclusion is in agreement with the results of earlier, optical rotation studies by Isbell and Pigman [64]. In contrast, for D-talose, the spectrum of the lyophilizate showed bands absent from the spectrum of either anomer of the pyranose form. These results also agreed with those of the earlier work [65] (namely, that the equilibrium mixture contains the α- and β-furanose forms), and have since been confirmed, and quantified, by n.m.r. spectroscopy [66].

5.2. Quantitative

Mutarotation of sugars has also been studied quantitatively. Parker [67] recorded the spectra, for the range of 6.00 to 11.00 μm (1667 to 909 cm^{-1}), of 20 percent aqueous solutions of α-D-glucose, β-D-glucose, and β-D-mannose: (a) 2.5 minutes after dissolution, and (b) at the end of mutarotation. By following the change in percent transmittance [at 8.75 μm (1143 cm^{-1}) for α- and β-D-glucose, and at 8.60 μm (1163 cm^{-1}) for β-D-mannose] with time, he was able to determine the mutarotation constants; these agreed well with those determined from measurements of change in optical rotation.

The intensity of a group frequency may be used for quantitative analysis, because it depends on the magnitude of the change in dipole moment that is associated with the molecular vibration. Consequently, strong bands are usually caused by the vibrations of polar linkages, such as O—H, N—H, C=O, C—N, etc. To a first approximation, the intensity of an absorption band characteristic of a specific group is proportional to the amount of that group present. Figure 5 shows part of the infrared spectra of equimolar solutions of three acetylated methyl glycopyranosides [17]. It may be seen that the area under the curve increases—from 3, to 4, to 5 acetyl groups. The procedure could be adapted for use as an analytical method—in this case, for acetyl; but any other group giving a characteristic band could similarly be analyzed for. In most cases, however, n.m.r. spectroscopy is a more convenient tool for such quantitative analysis, provided that a specific chemical-shift permits selected group integrations.

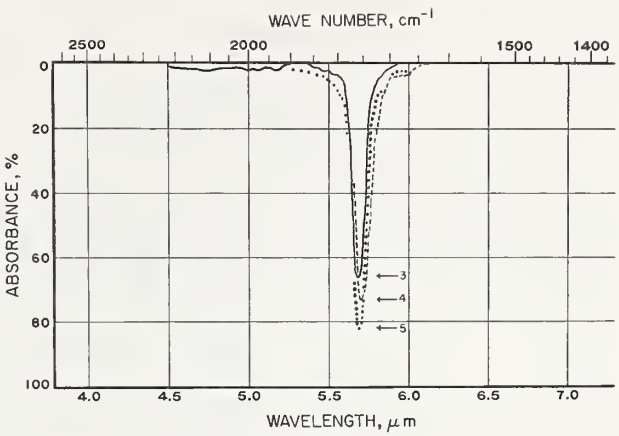
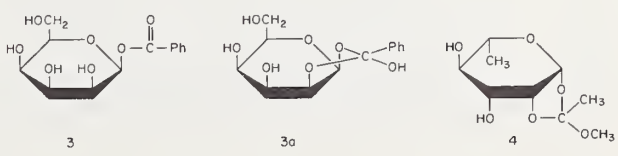


FIGURE 5. *Infrared spectra of methyl tri-*O*-acetyl-*α*-*L*-rhamnopyranoside (3), tetra-*O*-acetyl-*β*-*D*-mannopyranoside (4), and penta-*O*-acetyl-*D*-glycero-*β*-*D*-gulo-heptopyranoside (5). All solutions 0.0197* M *(3 and 5 in carbon tetrachloride; 4 in chloroform).*

(From Ref. [17].)

5.3. Determination of Structure

An example of solution of a structural problem involves the D-talose monobenzoate (**X**) obtained [65] as a byproduct from the action of peroxybenzoic acid on D-galactal. There seemed a possibility that it might be a 1,2-(orthobenzoate) (**3a**), and so, its spectrum was compared [68] with that of 1,2-*O*-(1-methoxylethylidene)-L-rhamnose (**4**). As may be seen from figure 6, the latter has no band at 5.77 μm (1733 cm^{-1}), whereas **X** has a strong ester-carbonyl absorption there. Hence, **X** is not an orthobenzoate but a benzoate; it was thought to be 1-*O*-benzoyl-α-D-talose, but was later [69] shown to be the β-D anomer (**3**).



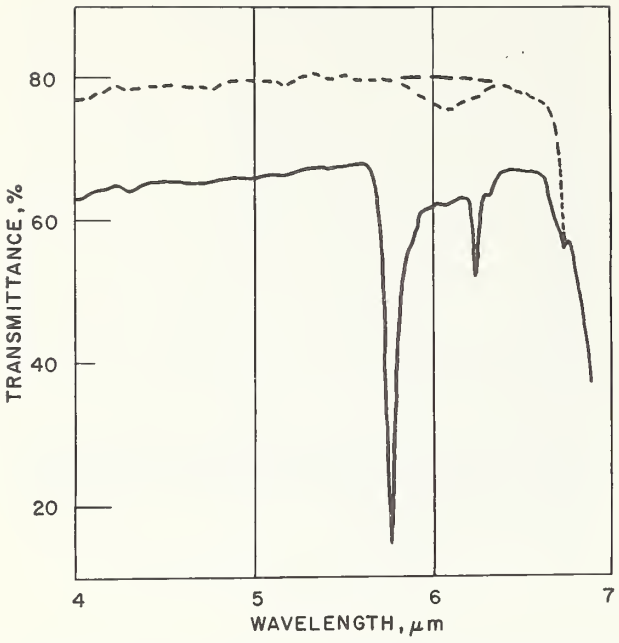
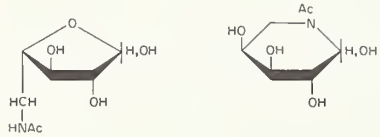


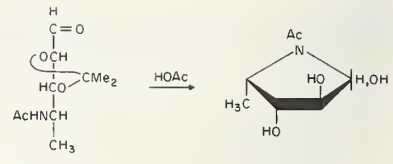
FIGURE 6. *Infrared spectra of 1,2-O-(1-methoxyethylidene)-L-rhamnose (– – – –) and 1-O-benzoyl-β-D-talopyranose (——) in potassium chloride pellets.*

(From Ref. [68].)

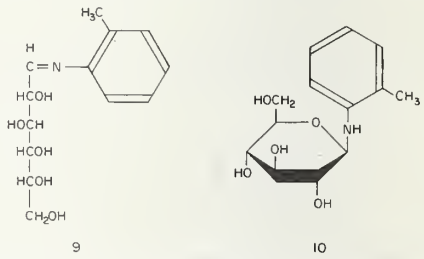
For sugars in which the hetero-atom of the ring may be nitrogen, the infrared spectra show immediately which form has this structure. For example, for the two ring-forms of 5-acetamido-5-deoxy-L-arabinose [70], one form shows bands at 3.03 μm (3300 cm^{-1}), 6.14 μm (1630 cm^{-1}), and 6.43 μm (1555 cm^{-1}), for OH and NH, NAc, and NH, respectively, and is therefore the furanose form (**5**), whereas the other form shows bands at 2.96 μm (3380 cm^{-1}) for OH, and 6.19 and 6.27 μm (1616 and 1595 cm^{-1}) for NAc, but no —NH— absorption near 6.43 μm (1555 cm^{-1}), and is therefore the pyranose (**6**).



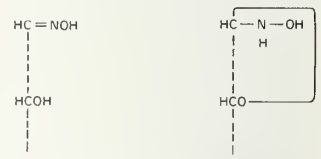
In another example, 4-acetamido-4,5-dideoxy-2,3-*O*-isopropylidene-*aldehydo*-L-xylose shows bands [71] at 3.10 μm (3226 cm^{-1}; NH), 5.81 μm (1721 cm^{-1}; CHO), 6.10 and 6.50 μm (1639 and 1538 cm^{-1}; NHAc), and 7.30 μm (1370 cm^{-1}; CMe_2). On treatment of this compound (**7**) with acetic acid, 4-acetamido-4,5-dideoxy-α,β-L-xylofuranose (**8**) was obtained; this compound (which cannot exist in a pyranoid form) shows C=O absorption at 6.12 μm (1634 cm^{-1}; Amide I).



The Schiff-base structure (**9**) was proposed [72] for *N*-*o*-tolyl-D-glucosylamine, because it shows a C=N band at 6.05 μm (1653 cm^{-1}). However, the pure compound shows [15] no band at 6.05 μm (1653 cm^{-1}), indicating that the structure is cyclic, probably the pyranoid form (**10**). All of the *N*-substituted glycosylamines examined by Ellis [15] were found, from their spectra, to have a cyclic structure.



The oximes of arabinose [72], rhamnose [72], and fructose [73] show a weak band at 6.05 μm (1653 cm^{-1}), which may indicate the acyclic form, but it is possible that the N—H of the cyclic form might



show a weak band of about the same frequency. D-Glucose oxime does not show a band in this region [72, 73], and is, presumably, cyclic. The acetyl derivatives of sugar oximes are undoubtedly cyclic, as they show the characteristic bands for the *N*-acetyl group [73].

Infrared spectroscopy has proved to be inappropriate for determining whether N^2-substituted hydrazones of sugars are cyclic or acyclic. Even for N^2-substituted hydrazones that are known to be acyclic, the intensity of the C=N band is so weak as to be unobservable [74]. Phenylosazones of sugars are known to exist preponderantly in the acyclic form, and they show [75] the C=N band at 6.3 μm (1587 cm^{-1}).

Acyclic semicarbazones usually show a band at 5.97 to 6.08 μm (1675 to 1645 cm^{-1}) for C=N. Acyclic thiosemicarbazones show a weak band at 6.06 to 6.14 μm (1650 to 1630 cm^{-1}); the thiosemicarbazones of seven aldoses did not show this band, and were therefore considered to have a cyclic structure [76].

Cellulose I, II, and III differ in the amorphous and crystalline regions, and their spectra show differences in the O—H stretching range. Thus, cellulose I shows [77] five bands in the OH region, and when cellulose film is treated [78, 79] with

deuterium oxide vapor, the intensity of one of these, at 2.78 to 3.03 μm (3600 to 3000 cm^{-1}), rapidly decreases and an O—D band at 3.70 to 4.17 μm (2700 to 2400 cm^{-1}) appears; the band affected is the OH stretching of the amorphous regions of the cellulose. The four bands that remain are those of hydrogen-bonded hydroxyl groups in the crystalline region. The ratio of the intensities of the OH and OD bands then gives an indication of the proportion of hydroxyl groups that are hydrogen-bonded in a crystalline manner, and this ratio thus provides a measure of the crystallinity [80].

The directions of the hydroxyl groups in celluloses were determined by using plane-polarized, infrared radiation [81] (see sec. 6). It was shown that the OH band at 3.02 μm (3309 cm^{-1}) is "perpendicular," and it was suggested that some of the hydroxyl bonds lie along the chain direction and form intramolecular hydrogen bonds.

The spectrum of starch indicates [82] that the hydroxyl groups are extensively hydrogen-bonded. The spectrum of potato starch differs from that of corn starch, especially in absorption regions for oxygen-containing groups. Thus, absorption is stronger [83] for the corn starch at 5.95 μm (1681 cm^{-1}), 9.5 to 10.5 μm (1053 to 952 cm^{-1}), and 11.7 μm (855 cm^{-1}), whereas it is stronger for potato starch at 10.8 μm (926 cm^{-1}). Arrow-root, corn, potato, rice, and wheat starches show bands at 3 μm (3333 cm^{-1}), 4.75 μm (2105 cm^{-1}), and 6.15 μm (1626 cm^{-1}). When the water content of the starch is changed, the band at 3 μm (3333 cm^{-1}) undergoes a change characteristic of the particular starch, and this property may be used for identifying and classifying starches [84].

6. Special Techniques

Plane-polarized radiation has proved useful in studying oriented films of such polysaccharides as cellulose, chitin, and xylan, providing information [81, 85] not given by other techniques. It has mainly been used in studying the crystal structure of samples having uniaxial orientation, as in fibers, in which the polymer chains are aligned along the fiber axis. The spectrum is measured with the radiation vector (a) parallel and (b) perpendicular to the chain direction. The respective intensity of the "parallel" and the "perpendicular" bands depends on the direction of the transition moment of the vibration responsible for the band, that is, whether it is mainly parallel or perpendicular to the chain direction. Thus, in the C—H stretching region of 3.33 to 3.57 μm (3000 to 2800 cm^{-1}) of the spectrum of cellulose, there are a number of partially overlapping bands some of which cannot be assigned on the basis of group-frequency. The C—H bonds of the ring are known to be approximately perpendicular to the chain axis, and so the dichroism of the bands associated with them must also be perpendicular; consequently, the perpendicular bands at *ca.* 3.45 μm (2900 cm^{-1}) have been assigned [86] to those vibrations. The cellulose band at 3.51 μm (2853 cm^{-1}) was assigned to the symmetrical stretch for CH_2, and a band at 7.00 μm (1430 cm^{-1}) to the CH_2 symmetrical bending mode.

The direction of the bonds in a crystal may also be determined. α-D-Glucopyranose shows one band at 2.94 μm (3405 cm^{-1}) and four others in the region of 2.99 to 3.12 μm (3347 to 3204 cm^{-1}). These have been correlated [79] with the results of x-ray diffraction studies, which show [55] that there is one O—H · · · O(C)(C) bond (between two molecules), and that there are four O—H · · · OH bonds. Similarly, the directions of the hydroxyl groups in sucrose have been determined [87].

The technique of attenuated total reflection [88] is useful for samples not amenable to examination by transmission spectroscopy; the radiation penetrates a short distance into the sample and is attenuated by absorption, and the extent of attenuation is independent of the thickness of the sample. For use with aqueous solutions, an attachment is placed in both beams of the spectrometer to compensate for absorption by water, making unnecessary the use of very thin, accurately matched cells to avoid interference by infrared absorption by water. The method has been applied [89] to the study of 20 carbohydrates in the region of 14.29 to 40.00 μm (700 to 250 cm^{-1}). For those compounds whose transmittance spectra in this region had previously been recorded [12, 13], the attenuated total reflection spectra were in good agreement. In this range, the anomers of a sugar afford different spectra.

The use of a micro-die for preparing alkali halide pellets, and of lead thiocyanate [which is water-soluble and gives a single band at 4.85 μm (2062 cm^{-1})] as an internal reference standard, permits identification and quantitative determination of micro quantities of water-soluble carbohydrates such as are obtained by paper chromatography [90].

Raman spectra, obtained with visible light, give the same kind of information as infrared spectra. The sample is irradiated with monochromatic light, and a very small fraction of the scattered light contains frequencies different from that of the source; these are characteristic of the molecule irradiated, and correspond closely in position, but not in intensity, to those in the infrared spectrum. For example, in the spectra of carboxylic acid dimers, the band for the C=O symmetrical stretching mode occurs strongly at ca. 6.02 μm (1660 cm^{-1}) in Raman spectra, but is very weak (not normally observed) in infrared spectra; in contrast, the band for the C=O asymmetrical stretching mode, at *ca.* 5.85 μm (1710 cm^{-1}), is weak in Raman, but very strong in infrared, spectra. Thus, Raman spectra supplement infrared spectra. Raman spectra have been

studied for some 1,3-dioxolane compounds related to sugar acetals [91]. Introduction of the technique of laser Raman spectroscopy may be expected to lead to greater activity in this field.

7. References

[1] For extensive treatments of the theory and practice of infrared spectroscopy, see: F. A. Miller, in Organic Chemistry, An Advanced Treatise (H. Gilman, Ed.), Vol. 3, Chapter 2, Wiley, New York, 1953; R. N. Jones and C. Sandorfy, in Chemical Applications of Spectroscopy; Technique of Organic Chemistry (W. West, Ed.), Vol. 9, Chapter 4, Interscience, New York, 1956; L. J. Bellamy, The Infra-red Spectra of Complex Molecules, 2nd ed., Wiley, New York, 1958; G. K. T. Conn and D. G. Avery, Infrared Methods: Principles and Applications, Academic Press, New York, 1960; K. Nakanishi, Practical Infrared Absorption Spectroscopy, Holden-Day, San Francisco, 1962; W. Brügel, An Introduction to Infrared Spectroscopy (translated from the German), Wiley, New York, 1962; W. J. Potts, Jr., Chemical Infrared Spectroscopy, Wiley, New York, 1963; C. N. R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York, 1963; A. D. Cross, Introduction to Practical Infrared Spectroscopy, 2nd ed., Butterworth, Washington, D.C., 1964; R. G. White, Handbook of Industrial Infrared Analysis, Plenum Press, New York, 1964; N. B. Colthup, L. H. Daly, and S. E. Wiberly, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1964; H. A. Szymanski, IR Theory and Practice of Infrared Spectroscopy, Plenum Press, New York, 1964; J. R. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, Prentice-Hall, Englewood Cliffs, N.J., 1965.

[2] R. S. Tipson, A. S. Cerezo, V. Deulofeu, and A. Cohen, J. Research NBS **71A,** 53 (1967).

[3] S. A. Barker, E. J. Bourne, and D. H. Whiffen, Methods Biochem. Anal. **3,** 213 (1956).

[4] R. S. Tipson, H. S. Isbell, and J. E. Stewart, J. Research NBS **62,** 257 (1959).

[5] L. P. Kuhn, J. Am. Chem. Soc. **74,** 2492 (1952); **76,** 4323 (1954).

[6] A. R. H. Cole and P. R. Jefferies, J. Chem. Soc. **1956,** 4391.

[7] S. A. Barker, J. S. Brimacombe, A. B. Foster, D. H. Whiffen, and G. Zweifel, Tetrahedron **7,** 10 (1959).

[8] V. C. Farmer, Spectrochim. Acta **8,** 374 (1957).

[9] V. C. Farmer, Chem. Ind. (London) **1959**, 1306.

[10] S. A. Barker, E. J. Bourne, H. Weigel, and D. H. Whiffen, Chem. Ind. (London) **1956**, 318.

[11] S. A. Barker, E. J. Bourne, W. B. Neely, and D. H. Whiffen, Chem. Ind. (London) **1954,** 1418.

[12] R. S. Tipson and H. S. Isbell, J. Research NBS **64A,** 239 (1960).

[13] R. S. Tipson and H. S. Isbell, J. Research NBS **66A,** 31 (1962).

[14] L. P. Kuhn, Anal. Chem. **22,** 276 (1950).

[15] G. P. Ellis, J. Chem. Soc. (B) **1966,** 572.

[16] American Petroleum Institute Project 44, Infrared Absorption Spectra, Data Distribution Office, Agricultural and Mechanical College of Texas, College Station, Texas 77843 (2440 spectra); American Society for Testing and Materials, 1916 Race St., Philadelphia, Pennsylvania 19103 (IBM cards; index to over 55,500 published spectra); The Documentation of Molecular Spectroscopy (DMS), Butterworth, Bethesda, Maryland 20014 (almost 200 sugar derivatives); H. M. Hershenson, Infrared Absorption Spectra, Indices for 1945–1957, and 1958–1962, Academic Press, New York, 1959 and 1964. National Research Council—National Bureau of Standards Catalog of Infrared Spectra and Bibliography, National Bureau of Standards, Washington, D.C. 20234 (punch cards), out of print; Ref. 2 [spectra of 23 *N*-glycosylacylamides and 21 1,1-bis(acylamido)-1-deoxyalditols]; Ref. 4 (28 cyclic acetals of sugars); Ref. 12 (24 aldopyranosides); Ref. 13 (6 anomeric pairs of sugars and 12 single anomers); Ref. 14 (79 carbohydrates); Sadtler Research Laboratories, 3316 Spring Garden St., Philadelphia, Pennsylvania 19104 (about 200 sugar derivatives); H. A. Szymanski, Infrared Band Handbook, Plenum Press, New York, Vol. 1 (1964), Supplements 1 and 2 (1964), Vol. 2 (1966), Supplements 3 and 4 (1966); R. L. Whistler and L. R. House, Anal Chem. **25,** 1463 (1953) (35 monosaccharides); J. W. White, Jr., C. R. Eddy, J. Petty, and N. Hoban, Anal. Chem. **30,** 506 (1958) (10 disaccharides and their acetates).

[17] H. S. Isbell, F. A. Smith, E. C. Creitz, H. L. Frush, J. D. Moyer, and J. E. Stewart, J. Research NBS **59,** 41 (1957); 56 sugar acetates.

[18] R. S. Tipson and H. S. Isbell, J. Research NBS **64A,** 405 (1960); 24 acetylated aldopyranosides.

[19] R. S. Tipson and H. S. Isbell, J. Research NBS **65A,** 31 (1961); 8 reducing pyranose acetates and 11 *N*-glycopyranosylacetamides.

[20] R. S. Tipson and H. S. Isbell, J. Research NBS **65A,** 249 (1961); 20 peracetylated pyranoses.

[21] T. Urbański, W. Hofmann, and M. Witanowski, Bull. Acad. Polon. Sci. Ser. Chim. Geol. Geograph. **7,** 619 (1959).

[22] D. H. Whiffen, Chem. Ind. (London) **1957,** 129.

[23] C. D. Hurd and H. Jenkins, Carbohyd. Res. **2,** 240 (1966).

[24] D. Horton and J. M. J. Tronchet, Carbohyd. Res. **2,** 315 (1966).

[25] H. B. Henbest, G. D. Meakins, B. Nicholls, and A. A. Wagland, J. Chem. Soc. **1957,** 1462.

[26] R. S. Tipson, J. Am. Chem. Soc. **74,** 1354 (1952).

[27] R. D. Guthrie and H. Spedding, J. Chem. Soc. **1960,** 953.

[28] R. S. Tipson and A. Cohen, Carbohyd. Res. **1,** 338 (1966).

[29] M. Stacey, R. H. Moore, S. A. Barker, H. Weigel, E. J. Bourne, and D. H. Whiffen, Proc. U.N. Intern. Conf. Peaceful Uses At. Energy, 2nd, Geneva, 1958, **20,** 251.

[30] J. S. Brimacombe, A. B. Foster, M. Stacey, and D. H. Whiffen, Tetrahedron **4,** 351 (1958).

[31] B. Åkermark, Acta Chem. Scand. **15,** 985 (1961).

[32] R. S. Tipson, W. S. Layne, and A. Cohen, unpublished results (1962).

[33] R. Kübler, W. Lüttke, and S. Weckberlin, Z. Elektrochem. **64,** 650 (1960); A. Rosenthal and M. R. S. Weir, J. Org. Chem. **28,** 3025 (1963).

[34] P. Bassignana and C. Cogrossi, Tetrahedron **20,** 2361 (1964).

[35] J. W. Rowen, F. H. Forziati, and R. E. Reeves, J. Am. Chem. Soc. **73,** 4484 (1951).

[36] H. Spedding, J. Chem. Soc. **1960,** 3147.

[37] M. L. Wolfrom and S. Hanessian, J. Org. Chem. **27,** 1800 (1962).

[38] S. F. D. Orr, R. J. C. Harris, and B. Sylvén, Nature **169,** 544 (1952); H. J. R. Stevenson and S. Levine, Science **116,** 705 (1952); S. Levine, H. J. R. Stevenson, and P. W. Kabler, Arch. Biochem. Biophys. **45,** 65 (1953).

[39] S. F. D. Orr, Biochim. Biophys. Acta **14,** 173 (1954).

[40] S. A. Barker, E. J. Bourne, R. M. Pinkard, and D. H. Whiffen, Chem. Ind. (London) **1958,** 658.

[41] See also, Y. Nitta, J. Ide, A. Momose, and M. Kawada, Yakugaku Zasshi **82,** 790 (1962); Chem. Abstr. **57,** 14601 (1962).

[42] R. Stephens, Ph. D. Thesis, University of Birmingham, England (1954).

[43] R. S. Tipson, J. Org. Chem. **26,** 2462 (1961).

[44] L. Hough, J. E. Priddle, R. S. Theobald, G. R. Barker, T. Douglas, and J. W. Spoors, Chem. Ind. (London) **1960,** 148.

[45] W. M. Doane, B. S. Shasha, E. I. Stout, C. R. Russell, and C. E. Rist, Abstr. Papers Am. Chem. Soc. Meeting **153,** 14c (1967).
[46] F. Micheel, F. P. van de Kamp, and H. Wulff, Chem. Ber. **88,** 2011 (1955).
[47] S. E. Darmon and K. M. Rudall, Discussions Faraday Soc. **9,** 251 (1950).
[48] D. Horton and M. L. Wolfrom, J. Org. Chem. **27,** 1794 (1962).
[49] A. G. Lloyd and K. S. Dodgson, Nature **184,** 548 (1959).
[50] K. Onodera, S. Hirano, and N. Kashimura, Carbohyd. Res. **1,** 208 (1965).
[51] E. Albano, D. Horton, and T. Tsuchiya, Carbohyd. Res. **2,** 349 (1966).
[52] F. A. Carey, D. H. Ball, and L. Long, Jr., Carbohyd. Res. **3,** 205 (1966).
[53] D. Horton and H. S. Prihar, Carbohyd. Res. **4,** 115 (1967).
[54] P. J. Launer, Perkin-Elmer Instr. News **13** (3), 10 (1962).
[55] T. R. R. McDonald and C. A. Beevers, Acta Cryst. **5,** 654 (1952).
[56] S. A. Barker, E. J. Bourne, M. Stacey, and D. H. Whiffen, J. Chem. Soc. **1954,** 171.
[57] S. A. Barker, E. J. Bourne, R. Stephens, and D. H. Whiffen, J. Chem. Soc. **1954,** 3468.
[58] S. A. Barker, E. J. Bourne, R. Stephens, and D. H. Whiffen, J. Chem. Soc. **1954,** 4211.
[59] S. A. Barker and R. Stephens, J. Chem. Soc. **1954,** 4550.
[60] L. M. J. Verstraeten, Anal. Chem. **36,** 1040 (1964). See also, *idem*, Carbohyd. Res. **1,** 481 (1966).
[61] C. J. Brown, Acta Cryst. **13,** 1049 (1960).
[62] A. G. Lloyd and K. S. Dodgson, Biochim. Biophys. Acta **46,** 116 (1961).
[63] D. A. Rees, J. Chem. Soc. **1963,** 1821.
[64] H. S. Isbell and W. W. Pigman, J. Research NBS **18.** 141 (1937).
[65] W. W. Pigman and H. S. Isbell, J. Research NBS **19.** 189 (1937).
[66] S. J. Angyal and V. A. Pickles, Carbohyd. Res. **4,** 269 (1967).
[67] F. S. Parker, Biochim. Biophys. Acta **42,** 513 (1960).
[68] H. S. Isbell, J. E. Stewart, H. L. Frush, J. D. Moyer, and F. A. Smith, J. Research NBS **57,** 179 (1956).
[69] H. B. Wood, Jr., and H. G. Fletcher, Jr., J. Am. Chem. Soc. **79,** 3234 (1957).
[70] J. K. N. Jones and J. C. Turner, J. Chem. Soc. **1962,** 4699.
[71] A. E. El-Ashmawy and D. Horton, Carbohyd. Res. **1,** 164 (1965).
[72] F. Legay, Compt. Rend. **234,** 1612 (1952).
[73] H. Bredereck, A. Wagner, D. Hummel, and H. Kreiselmeier, Chem. Ber. **89,** 1532 (1956).
[74] J. Fabian and M. Legrand, Bull. Soc. Chim. France **23,** 1461 (1956); J. Fabian, M. Legrand, and P. Poirier, ibid. **23,** 1499 (1956).
[75] W. Otting, Ann. **640,** 44 (1961).
[76] J. R. Holker, cited in H. Spedding, Advan. Carbohydrate Chem. **19,** 23 (1964); see p. 40 and footnote 51 on p. 37.
[77] L. Brown, P. Holliday, and I. F. Trotter, J. Chem. Soc. **1951,** 1532.
[78] K. E. Almin, Svensk Papperstid. **55,** 767 (1952).
[79] H. J. Marrinan and J. Mann, J. Appl. Chem. (London) **4,** 204 (1954).
[80] J. Mann and H. J. Marrinan, Trans. Faraday Soc. **52,** 481, 487, 492 (1956).
[81] J. Mann and H. J. Marrinan, J. Polymer Sci. **27,** 595 (1958); **32,** 357 (1958); M. Tsuboi, ibid. **25,** 159 (1957).
[82] M. Samec, Stärke **5,** 105 (1953).
[83] M. Samec, J. Polymer Sci. **23,** 801 (1957).
[84] O. Yovanovitch, Compt. Rend. **252,** 2884 (1961).
[85] C. Y. Liang and R. H. Marchessault, J. Polymer Sci. **37,** 385 (1959); **39,** 269 (1959); **43,** 85 (1960); F. G. Pearson, R. H. Marchessault, and C. Y. Liang, ibid. **43,** 101 (1960); R. H. Marchessault and C. Y. Liang, ibid. **43,** 71 (1960); **59,** 357 (1962); R. H. Marchessault, F. G. Pearson, and C. Y. Liang, Biochim. Biophys. Acta **45,** 499 (1960).
[86] R. H. Marchessault, Pure Appl. Chem. (London) **5,** 107 (1962).
[87] J. W. Ellis and J. Bath, J. Chem. Phys. **6,** 221 (1938).
[88] J. Fahrenfort, Spectrochim. Acta **17,** 698 (1961).
[89] F. S. Parker and R. Ans, Appl. Spectry. **20,** 384 (1966).
[90] F. E. Resnik, L. S. Harrow, J. C. Holmes, M. E. Bill, and F. L. Greene, Anal. Chem. **29,** 1874 (1957).
[91] S. A. Barker, E. J. Bourne, R. M. Pinkard, and D. H. Whiffen, J. Chem. Soc. **1959,** 802, 807.

U.S. GOVERNMENT PRINTING OFFICE : 1967—O-290-632

NBS TECHNICAL PUBLICATIONS

PERIODICALS

JOURNAL OF RESEARCH reports National Bureau of Standards research and development in physics, mathematics, chemistry, and engineering. Comprehensive scientific papers give complete details of the work, including laboratory data, experimental procedures, and theoretical and mathematical analyses. Illustrated with photographs, drawings, and charts.

Published in three sections, available separately:

• Physics and Chemistry

Papers of interest primarily to scientists working in these fields. This section covers a broad range of physical and chemical research, with major emphasis on standards of physical measurement, fundamental constants, and properties of matter. Issued six times a year. Annual subscription: Domestic, $5.00; foreign, $6.00*.

• Mathematical Sciences

Studies and compilations designed mainly for the mathematician and theoretical physicist. Topics in mathematical statistics, theory of experiment design, numerical analysis, theoretical physics and chemistry, logical design and programming of computers and computer systems. Short numerical tables. Issued quarterly. Annual subscription: Domestic, $2.25; foreign, $2.75*.

• Engineering and Instrumentation

Reporting results of interest chiefly to the engineer and the applied scientist. This section includes many of the new developments in instrumentation resulting from the Bureau's work in physical measurement, data processing, and development of test methods. It will also cover some of the work in acoustics, applied mechanics, building research, and cryogenic engineering. Issued quarterly. Annual subscription: Domestic, $2.75; foreign, $3.50*.

TECHNICAL NEWS BULLETIN

The best single source of information concerning the Bureau's research, developmental, cooperative and publication activities, this monthly publication is designed for the industry-oriented individual whose daily work involves intimate contact with science and technology—*for engineers, chemists, physicists, research managers, product-development managers, and company executives.* Annual subscription: Domestic, $1.50; foreign, $2.25*.

*Difference in price is due to extra cost of foreign mailing.

NONPERIODICALS

Applied Mathematics Series. Mathematical tables, manuals, and studies.

Building Science Series. Research results, test methods, and performance criteria of building materials, components, systems, and structures.

Handbooks. Recommended codes of engineering and industrial practice (including safety codes) developed in cooperation with interested industries, professional organizations, and regulatory bodies.

Special Publications. Proceedings of NBS conferences, bibliographies, annual reports, wall charts, pamphlets, etc.

Monographs. Major contributions to the technical literature on various subjects related to the Bureau's scientific and technical activities.

National Standard Reference Data Series. NSRDS provides quantitative data on the physical and chemical properties of materials, compiled from the world's literature and critically evaluated.

Product Standards. Provide requirements for sizes, types, quality and methods for testing various industrial products. These standards are developed cooperatively with interested Government and industry groups and provide the basis for common understanding of product characteristics for both buyers and sellers. Their use is voluntary.

Technical Notes. This series consists of communications and reports (covering both other agency and NBS-sponsored work) of limited or transitory interest.

CLEARINGHOUSE

The Clearinghouse for Federal Scientific and Technical Information, operated by NBS, supplies unclassified information related to Government-generated science and technology in defense, space, atomic energy, and other national programs. For further information on Clearinghouse services, write:

Clearinghouse
U.S. Department of Commerce
Springfield, Virginia 22151

Order NBS publications from:
Superintendent of Documents
Government Printing Office
Washington, D.C. 20402

UNITED STATES
GOVERNMENT PRINTING OFFICE
DIVISION OF PUBLIC DOCUMENTS
WASHINGTON, D.C. 20402

OFFICIAL BUSINESS

POSTAGE AND FEES PAID
U.S. GOVERNMENT PRINTING OFFICE